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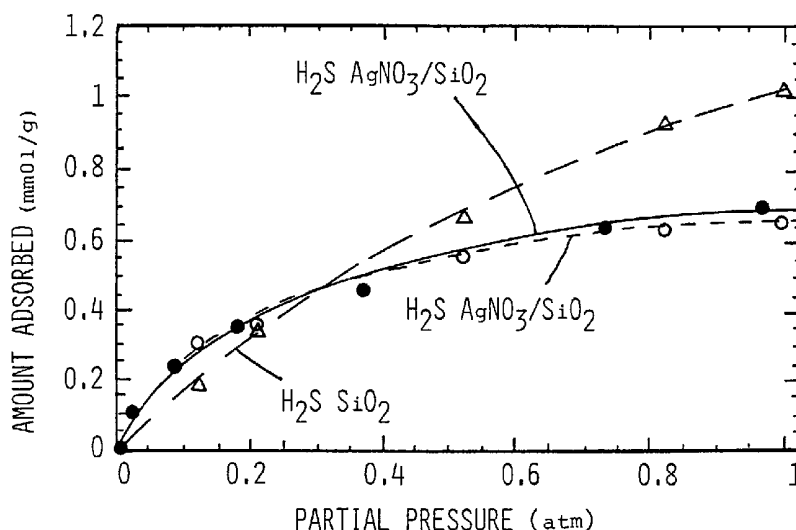
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(54) Title: SULFUR RESISTANT ADSORBENTS



(57) Abstract: Sulfur resistant/tolerant adsorbents useful for separating olefins from paraffins in a cracked gas stream including hydrogen sulfide. The method comprises the steps of contacting the gaseous mixture with an adsorbent which preferentially adsorbs the alkene, at a selected temperature and pressure, thereby producing a nonadsorbed component and an alkene-rich adsorbed component; the adsorbent comprising a carrier having a surface area, the carrier having a monolayer of a silver compound or a copper compound, the silver or copper compound releasably retaining the alkene; and changing at least one of the pressure and temperature to thereby release the alkene-rich component from the adsorbent. The adsorbent substantially maintains its adsorbent capacity and preference for the alkene in the presence of the sulfur compound. Sulfur resistant/tolerant adsorbents useful for selectively separating dienes from a mixture, particularly one containing mono-olefins and hydrogen sulfide, are also disclosed.



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SULFUR RESISTANT ADSORBENTS

BACKGROUND OF THE INVENTION

5 The present invention relates generally to adsorbents for selectively separating olefins from paraffins, and to adsorbents for selectively separating dienes from a mixture, particularly one containing mono-olefins. More particularly, the present invention relates to such adsorbents which are resistant to and/or tolerant of sulfur poisoning.

10 Petroleum is an extremely complex mixture and consists predominantly of hydrocarbons, as well as compounds containing nitrogen, oxygen, and sulfur. Most petroleums also contain minor amounts of nickel and vanadium. The chemical and physical properties of petroleum vary considerably because of the variations in composition.

15 The ultimate analysis (elemental composition) of petroleum tends to vary over relatively narrow limits -- carbon: 83.0 to 87.0 percent; hydrogen: 10.0 to 14.0 percent; nitrogen: 0.1 to 1.5 percent; oxygen: 0.1 to 1.5 percent; sulfur: 0.1 to 5.0 percent; metals (nickel plus vanadium): 10 to 500 ppm.

20 Crude oils are seldom used as fuel because they are more valuable when refined to petroleum products. Distillation separates the crude oil into fractions equivalent in boiling range to gasoline, kerosine, gas oil, lubricating oil, and residual. Thermal or catalytic cracking is used to convert kerosine, gas oil, or residual to gasoline, lower-boiling fractions, and a residual coke. Petrochemical intermediates such as ethylene and propylene are primarily produced by the thermal cracking of light hydrocarbon feedstocks in the presence of steam. Catalytic reforming,
25 isomerization, alkylation, polymerization, hydrogenation, and combinations of these catalytic processes are used to upgrade the various refinery intermediates into improved gasoline stocks or distillates. The major finished products are usually blends of a number of stocks, plus additives.

30 Gasoline is a complex mixture of hydrocarbons that distills within the range 100 to 400°F. Commercial gasolines are blends of straight-run, cracked, reformed, and natural gasolines. Straight-run gasoline is recovered from crude petroleum by distillation and contains a large proportion of normal hydrocarbons of

the paraffin series. Cracked gasoline is manufactured by heating crude-petroleum distillation fractions or residues under pressure, or by heating with or without pressure in the presence of a catalyst. Heavier hydrocarbons are broken into smaller molecules, some of which distill in the gasoline range. Reformulated gasoline is made
5 by passing gasoline fractions over catalysts in such a manner that low-octane-number hydrocarbons are molecularly rearranged to high-octane-number components. Many of the catalysts use platinum and other metals deposited on a silica and/or alumina support. Natural gasoline is obtained from natural gas by liquefying those constituents which boil in the gasoline range either by compression and cooling or by
10 absorption in oil.

Propylene is recovered as a by-product in the catalytic cracking of gas oils to gasoline. Catalytic cracking is a low-pressure process which normally operates at 450-600°C with a strongly acidic catalyst containing a crystalline aluminosilicate (molecular sieve). Cracking of paraffinic components proceeds by a
15 carbonium ion mechanism which has a β -fission step similar to that found for free radicals. Lower olefins are also recovered to a lesser extent from Fisher-Tropsch, thermal-cracking and coal-gasification units.

The presence of sulfur compounds is generally known to have deleterious effects in various petroleum refining processes. For example, in catalytic
20 reforming, the catalyst used is often platinum supported on high-purity alumina. However, the platinum on the catalyst is seriously deactivated by sulfur compounds, and therefore the feedstock is desulfurized to less than 3 ppm by weight of sulfur before the reforming. See, for example, Tedder, J.M., A. Nechvatal and A.H. Jubb, Basic Organic Chemistry, Part 5: Industrial Products, Chapter 3.2, "Preparation of
25 Primary Petrochemicals: Reforming," pp. 53-60 (1975).

U.S. Patent No. 6,063,723 issued to Miller also demonstrates that sulfur is known to have deleterious effects. The '723 patent discloses a sulfur tolerant zeolite catalyst for use in catalytic dehydrogenation of light paraffinic hydrocarbons. This catalyst is prepared such that it has a very specific alkali to aluminum ratio in
30 the zeolite. Although this patent's disclosed sulfur tolerance is better than that of

previously known catalysts, it is still only disclosed to be tolerant of sulfur in the range of up to 2 ppm sulfur, and more preferably up to 0.5 ppm sulfur.

Cracked gas streams include a blend of many components, including olefins, paraffins, H_2 , H_2S , etc. The cracked gas streams are first subjected to caustic
5 scrubbing in order to remove hydrogen sulfide. Then, it is necessary to separate olefins from paraffins in these streams in order to obtain a product rating. Conventional methods for such separation include multiple distillation runs, one of which removes, for example, H_2 and methane. Thereafter, the stream includes C_2 's and higher, mixed with olefins and paraffins. This stream is then distilled to separate
10 the olefins from the paraffins. However, this distillation is very energy intensive and difficult to accomplish because of relatively close volatilities when alkene\alkane (olefin\paraffin) separation is required. For example, ethane\ethylene separation is carried out at about $-25^\circ C$ and 320 psig (2.603 MPa) in a column containing over 100 trays, and propane\propylene separation is performed by an equally energy-
15 intensive distillation at about $38^\circ C$ and 260 psig (1.8 MPa). It is evident that high capital costs and high operational costs are incurred in any cryogenic distillation approach.

Further, it is also very difficult to separate a diene from a mixture, particularly one containing mono-olefin. Purifying the mono-olefin, 1-butene, is
20 particularly troublesome due to the closeness of its boiling point to that of 1,3-butadiene. In order to increase the purity of 1-butene, it is necessary to separate it from other hydrocarbons. Ordinarily, fractionation alone is cost prohibitive for completely separating 1,3-butadiene to achieve the desired purity of 1-butene in these mixtures. Presently, butadiene is separated from olefins and paraffins primarily by
25 distillation with selective solvents and by absorption using solutions of absorbents. Extractive distillation is relatively energy-intensive, complex and not economical. There are several drawbacks, in that this puts water vapor and/or solvent vapor into the regenerated product. Further, metal salts often are instable in solution and will precipitate out of solution. Selective absorption with metal salt solution involves
30 additional stages with recycling of streams between stages to remove water vapor

and/or solvent vapor from the regenerated product. This method has the disadvantage of being energy-intensive and requiring handling and recirculating of solvent streams which themselves contain contaminants or are subject to degradation. Current processes for olefin\paraffin separation have not been sufficiently selective to economically achieve the desired result for purifying mixtures of unsaturated hydrocarbons.

Thus, it would be desirable to provide adsorbents which would cost-effectively and successfully achieve separation of olefins from paraffins. It would further be desirable to provide adsorbents which would cost-effectively and successfully achieve separation of dienes from mono-olefins. Still further, it would be desirable to provide such adsorbents which are advantageously resistant to and/or tolerant of sulfur poisoning.

SUMMARY OF THE INVENTION

The present invention addresses and solves the above-mentioned problems, as well as others not enumerated, by providing novel, sulfur resistant and/or tolerant adsorbents useful in a method of separating gaseous alkene selected from the group consisting of ethylene, propylene and mixtures thereof, from a gaseous mixture including the alkene and a sulfur compound. The method comprises the steps of contacting the gaseous mixture with an adsorbent which preferentially adsorbs the alkene, at a selected temperature and pressure, thereby producing a non-adsorbed component and an alkene-rich adsorbed component; the adsorbent comprising a carrier having a surface area, the carrier having been impregnated with a silver or copper compound by incipient wetness or other suitable method, thereby resulting in a monolayer of the silver or copper compound dispersed on substantially the entire surface area, the silver compound releasably retaining the alkene; and the carrier comprising a plurality of pores having a pore size greater than the effective molecular diameter of the alkene; and changing at least one of the pressure and temperature to thereby release the alkene-rich component from the adsorbent. The adsorbent advantageously and unexpectedly substantially maintains its adsorbent capacity and preference for the alkene in the presence of the sulfur compound.

Further novel, sulfur resistant and/or tolerant adsorbents are useful in a method for separating a diene from a mixture including the diene and a sulfur compound. The process comprises the step of contacting the mixture with an adsorbent which preferentially adsorbs the diene, at a selected temperature and pressure, thereby producing a non-adsorbed component and a diene-rich adsorbed component, wherein the adsorbent comprises an ion-exchanged zeolite selected from the group consisting of zeolite X, zeolite Y, zeolite LSX, and mixtures thereof, the zeolite having exchangeable cationic sites, and at least some, perhaps a majority, of the sites having silver cation or copper cation present, and wherein the preferential adsorption occurs by π -complexation, and further wherein the adsorbent advantageously and unexpectedly substantially maintains its adsorbent capacity and preference for the diene in the presence of the sulfur compound.

BRIEF DESCRIPTION OF THE DRAWINGS

Other objects, features and advantages of the present invention will become apparent by reference to the following detailed description and drawings, in which:

Fig. 1 is a graph showing comparison of H_2S adsorption on SiO_2 and $\text{AgNO}_3/\text{SiO}_2$ at 70°C ;

Fig. 2 is a graph showing H_2S effect on olefin adsorption on $\text{AgNO}_3/\text{SiO}_2$;

Fig. 3 is a graph showing C_2H_4 cyclic adsorption on $\text{AgNO}_3/\text{SiO}_2$ at 50°C ;

Fig. 4 is a graph showing C_3H_6 cyclic adsorption on $\text{AgNO}_3/\text{SiO}_2$ at 50°C ;

Fig. 5 is a graph showing C_3H_6 cyclic adsorption on $\text{AgNO}_3/\text{SiO}_2$ at 120°C ;

Fig. 6 is a graph showing H_2S adsorption and desorption on SiO_2 at 298K;

Fig. 7 is a graph showing H_2S adsorption and desorption on $\text{AgNO}_3/\text{SiO}_2$ at 298K;

Fig. 8 is a graph showing H₂S adsorption and desorption on AgNO₃/SiO₂ at 343K;

Fig. 9 is a graph showing the effect of H₂S poisoning on AgNO₃/SiO₂ capacity for C₃H₆ at 343K;

5 Figs. 10a and 10b are graphs showing isotherms of 1,3-butadiene and 1-butene at 120°C;

Fig. 11 is a graph showing Ag-Y after H₂S exposure vs. Na-Y before H₂S exposure;

10 Fig. 12a is an isotherm of 1,3-butadiene before and after H₂S exposure;

Fig. 12b is an isotherm of 1-butene before and after H₂S exposure;

Fig. 12c is a table showing calculated heat of adsorption of 1,3-butadiene and 1-butene before and after H₂S exposure;

15 Fig. 13 is a graph showing cumulative pore volume of Ag-Y before and after H₂S exposure;

Figs. 14a and 14b are fractional uptake curves of 1-butene and 1,3-butadiene before and after H₂S exposure;

Fig. 14c is a table showing diffusion time constants for 1,3-butadiene and 1-butene before and after H₂S exposure;

20 Fig. 15 is a graph showing an isotherm of benzene and 1-hexene on Ag-Y;

Fig. 16 is a graph showing H₂S isotherms on Ag-Y;

Fig. 17 is a graph showing isotherms of C₄H₆ and C₄H₈ on Ag-Y at 120°C;

25 Fig. 18 is a graph showing isotherms of 1,3-butadiene before and after H₂S exposure at 120°C;

Fig. 19 is a graph showing isotherms of 1-butene before and after H₂S exposure at 120°C;

30 Fig. 20 is a graph showing isotherms of 1-butene and 1,3-butadiene before and after H₂S exposure;

Fig. 21 shows equilibrium isotherms of C_2H_4 and C_2H_6 at $70^\circ C$ on SiO_2 and $AgNO_3/SiO_2$ prepared via thermal monolayer (monomolecular layer) dispersion method at $70^\circ C$. Lines are fittings with eqs. (A) and (B);

Fig. 22 shows equilibrium isotherms of C_2H_4 and C_2H_6 at $70^\circ C$ on $AgNO_3/SiO_2$ prepared via incipient wetness impregnation method. Lines are fittings with eqs. (A) and (B);

Fig. 22A shows equilibrium isotherms of C_2H_4 and C_2H_6 at $25^\circ C$ on $AgNO_3/SiO_2$ sorbent. This sorbent was prepared by impregnating SiO_2 with the $AgNO_3$, using incipient wetness technique to achieve a monomolecular layer of the Ag salt on the SiO_2 carrier;

Fig. 23 shows equilibrium isotherms of C_3H_6 at $25^\circ C$ on AgX/SiO_2 via thermal monolayer dispersion method;

Fig. 24 shows normalized C_3H_6 equilibrium data at $25^\circ C$ on AgX/SiO_2 via thermal monolayer dispersion method;

Fig. 25 shows equilibrium isotherms of C_3H_6 at $70^\circ C$ on incipient wetness impregnated $AgNO_3/\gamma-Al_2O_3$, $AgNO_3/SiO_2$ and $AgNO_3/MCM-41$. Lines are fitting with eq. (B);

Fig. 26 shows selective adsorption of C_3H_6 over C_3H_8 at $70^\circ C$ on incipient wetness impregnated $AgNO_3/SiO_2$. Lines are fittings with eqs. (A) and (B);

Fig. 27 shows normalized C_3H_6 equilibrium data at $70^\circ C$ on incipient wetness impregnated $AgNO_3/\gamma-Al_2O_3$, $AgNO_3/SiO_2$ and $AgNO_3/MCM-41$;

Fig. 28 shows sequence and basic steps in the four-step PSA cycle;

Fig. 29 shows equilibrium C_2H_4 and C_2H_6 isotherms on zeolite 4A at 25° and $70^\circ C$. For all isotherm figures, symbols are experimental data and lines are fitted isotherms;

Fig. 30 shows uptake curves of C_2H_4 and C_2H_6 on zeolite 4A at 25° and $70^\circ C$ at $P = 0-0.1$ atm;

Fig. 31 shows equilibrium isotherms of C_3H_6 and C_3H_8 on zeolite 4A at 25° and $120^\circ C$;

Fig. 32 shows uptake rates of C_3H_6 on zeolite 4A at 25° and $120^\circ C$;

Fig. 33 shows equilibrium isotherms of C_2H_4 and C_2H_6 on molecular-sieve carbon at 25° and 100°C;

Fig. 34 shows equilibrium isotherms of C_3H_6 and C_3H_8 on monolayer $AgNO_3/SiO_2$ at 25° and 70°C;

5 Fig. 35 shows C_2H_4 product purity (%) vs. C_2H_4 product recovery (%) for PSA using zeolite 4A and Ag^+ -exchanged Amberlyst-35 resin at average C_2H_4 product throughput = 1.1×10^{-4} kg of product/h/kg of adsorbent. Feed temperature = 25°C. Inset figures refer to the number of the corresponding run shown in Table 4;

10 Fig. 36 shows C_3H_6 product throughput vs. C_3H_6 % product recovery in this case of zeolite 4A and monolayer $AgNO_3/SiO_2$ at 99.1% C_3H_6 product purity. Feed temperature for zeolite 4A and $AgNO_3/SiO_2$ sorbents is 100°C and 70°C, respectively. Inset figures refer to the number of the corresponding run shown in Table 5;

15 Fig. 37 shows transient behavior of C_3H_6 concentration in the desorption product from step 4 as system approaches cyclic steady state at different feed velocities starting from a bed saturated with 5% C_3H_6 and 95% C_3H_8 at 0.1 atm in the case of $AgNO_3/SiO_2$ sorbent. $P_H = 1.0$ atm; $P_L = 0.1$ atm; step time = 210 s; purge velocity = 0.186 cm/s; feed temperature = initial temperature = 70°C;

20 Fig. 38 shows multiplicity in PSA cyclic steady states with $AgNO_3/SiO_2$. Effect of interstitial feed velocity U_H , on the C_3H_6 concentration in the desorption (step 4) product. The lower branch started with initial temperature of 70°C, while the upper branch started with that of 120°C. $P_H = 1.0$ atm; $P_L = 0.1$ atm; step time 210 s; purge velocity = 0.186 cm/s; feed temperature = 70°C;

25 Fig. 39 shows transient behavior of C_3H_6 concentration in the desorption product from step 4 as system approaches cyclic steady state at different purge velocities starting from a bed saturated with 5% C_3H_6 and 95% C_3H_8 at 0.1 atm in the case of $AgNO_3/SiO_2$ sorbent.

30 Feed temperature = initial temperature = 70°C. $P_H = 1.0$ atm; $P_L = 0.1$ atm; step time 210 s; feed velocity = 0.80 cm/s;

Fig. 40 shows multiplicity in PSA cyclic steady states with $\text{AgNO}_3/\text{SiO}_2$. Effect of interstitial purge velocity, Up , on the C_3H_6 concentration in the desorption (step 4) product. The lower branch started with initial temperature of 70°C while the upper branch started with that of 120°C . $P_H = \text{atm}$; $P_L = 0.1 \text{ atm}$; step
 5 time 210 s; feed velocity = .80 cm/s; feed temperature = 70°C ;

Fig. 41 shows line representations of zeolite structure: (A) solidate cage, or truncated octahedron; (B) type A zeolite "unit cell"; (C) "unit cell" of types X and Y, or faujasite; (D) cation sites in type A (there are eight I, three II, and twelve
 10 III sites per unit cell); (E) cation sites in types X and Y (16 I, 32 I', 32 II, 32 II', 48 III, and 32 III' sites per unit cell);

Fig. 42 shows the pure-component equilibrium isotherms of 1,3- C_4H_6 and 1- C_4H_8 on NaY and NaLSX type zeolites at 70°C ;

Fig. 43 shows uptake curves for 1,3- C_4H_6 and 1- C_4H_8 on NaY-type zeolites;

15 Fig. 44 shows the pure component equilibrium isotherms for 1,3- C_4H_6 and 1- C_4H_8 AgY zeolite at 70°C and 25°C ;

Fig. 45 shows the equilibrium isotherms of C_2H_4 on NaY and AgY type zeolites at 70°C ;

20 Fig. 46 shows low pressure equilibrium isotherms for 1,3- C_4H_6 and 1- C_4H_8 on 5A zeolite at 25°C ;

Fig. 47 shows uptake curves for 1,3- C_4H_6 and 1- C_4H_8 on Sr exchanged 5A and 5A zeolites measured at 70°C ;

Fig. 48 shows desorption curve for temperature driven release of 1,3- C_4H_6 from 5A zeolite;

25 Fig. 49 shows equilibrium adsorption isotherms for C_4H_6 on AgY and NaY at 120°C ; and

Fig. 50 shows low pressure equilibrium isotherms for 1,3- C_4H_6 and 1- C_4H_8 on 5A at 70°C .

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

As disclosed hereinabove, it has been generally expected that adsorbents containing metal compounds would be irreversibly poisoned and rendered useless upon prolonged and/or extensive exposure to sulfur containing compounds, such as for example, hydrogen sulfide. However, in the present invention, novel adsorbents useful for cost-effective and highly successful separation of olefins from paraffins, and separation of dienes from a mixture (particularly one containing mono-olefins) have been unexpectedly and fortuitously discovered to be tolerant of and/or resistant to sulfur compounds. These inventive adsorbents have been shown to substantially maintain their selectivity and their adsorption capacity, even upon severe exposure to H₂S.

In one embodiment of the present invention, there is disclosed a novel method of separating gaseous alkene selected from the group consisting of ethylene, propylene and mixtures thereof, from a gaseous mixture including the alkene and a sulfur compound. The method comprises the step of contacting the gaseous mixture with an adsorbent which preferentially adsorbs the alkene, at a selected temperature and pressure, thereby producing a non-adsorbed component and an alkene-rich adsorbed component.

The adsorbent comprises a carrier having a surface area, the carrier having been impregnated with a silver or copper compound by incipient wetness or other suitable method, thereby resulting in a monolayer of the silver or copper compound dispersed on substantially the entire surface area. The silver or copper compound releasably retains the alkene; and the carrier comprises a plurality of pores having a pore size greater than the effective molecular diameter of the alkene.

There are several methods for accomplishing dispersion of the metal compound onto a carrier or support. These methods include thermal monolayer dispersion, impregnation by incipient wetness technique, and spray application. In a preferred embodiment, the adsorbent of the invention is prepared by dispersing the metal compound onto the carrier under conditions that do not decompose or oxidize the compound. It is preferred that the dispersion permits the chemical compound to

retain its character. The impregnation by incipient wetness technique accomplishes these objectives. This technique avoids decomposition of the metal compound which is more likely to occur by thermal dispersion heating method. Further, incipient wetness technique permits the defective dispersion of a monomolecular layer of metal compound on the carrier.

It is to be understood that any suitable carrier may be used. However, in a preferred embodiment, the carrier has a BET surface area greater than about 50 square meters per gram and up to about 2,000 square meters per gram, and comprises a plurality of pores having a pore size greater than about 3 angstroms and up to about 10 microns. In a more preferred embodiment, the carrier is a high surface area support selected from the group consisting of refractory inorganic oxide, molecular sieve, activated carbon, and mixtures thereof. Still more preferred, the carrier is a refractory inorganic oxide selected from the group consisting of pillared clay, alumina and silica.

It is also to be understood that any suitable silver or copper compound may be used. In a preferred embodiment, the silver compound is a silver (I) halide. In a more preferred embodiment, the silver compound is a silver salt, and the salt is selected from the group consisting of acetate, benzoate, bromate, chlorate, perchlorate, chlorite, citrate, fluoride, nitrate, nitrite, sulfate, and mixtures thereof.

In one exemplary embodiment of this embodiment of the present invention, the silver compound is silver nitrate (AgNO_3) and the carrier is silica (SiO_2).

The method of the present invention may further comprise the step of changing at least one of the pressure and temperature to thereby release the alkene-rich component from the adsorbent. It is to be understood that the pressures and temperatures used may be within a suitable range. However, in the preferred embodiment, the selected pressure of preferential adsorption is a first pressure, and the pressure of release is a second pressure less than the first pressure. In a more preferred embodiment, the first pressure is in a range of about 1 atmosphere to about

35 atmospheres, and the second pressure is in a range of about 0.01 atm to about 5 atm.

In the preferred embodiment, the selected temperature of preferential adsorption is a first temperature, and the temperature of release is a second
5 temperature greater than the first temperature. In a more preferred embodiment, the first temperature is in a range of about 0°C to about 50°C, and the second temperature is in a range of about 70°C to about 200°C.

Without being bound to any theory, it is believed that the retaining of the alkene is accomplished by formation of π -complexation bonds between the silver
10 or copper compound and the alkene. Separation by π -complexation is a subgroup of chemical complexation where the mixture is contacted with a second phase, which contains a complexing agent. The advantage of chemical complexation is that the bonds formed are stronger than those by van der Waals forces alone, so it is possible to achieve high selectivity and high capacity for the component to be bound. At the
15 same time, the bonds are still weak enough to be broken by using simple engineering operations such as raising the temperature or decreasing the pressure.

The π -complexation generally pertains to the main group (or d-block) transition metals, that is, from Sc to Cu, Y to Ag, and La to Au in the periodic table. These metals or their ions can form the normal σ bond to carbon and, in addition, the
20 unique characteristics of the d orbitals in these metals or ions can form bonds with the unsaturated hydrocarbons (olefins) in a nonclassic manner. This type of bonding is broadly referred to as π -complexation, and has been considered for gaseous hydrocarbon separation and purification using cumbersome liquid solutions. It has been unexpectedly and fortuitously discovered, however, that of the transition metals,
25 copper and silver may be substantially more effective in the subject separations than are the other transition metals.

As demonstrated further hereinbelow, this novel adsorbent fortuitously and unexpectedly substantially maintains its adsorbent capacity and preference for the alkene in the presence of the sulfur compound. This is highly
30 desirable, as this sulfur tolerant and/or resistant adsorbent (as well as the other novel

adsorbents described hereinbelow) obviates step(s) conventionally necessary to desulfurize the cracked gas stream(s).

In a further embodiment, a novel method is disclosed for separating a diene from a mixture including the diene and a sulfur compound. The process
5 comprises the step of contacting the mixture with an adsorbent which preferentially adsorbs the diene, at a selected temperature and pressure, thereby producing a non-adsorbed component and a diene-rich adsorbed component. The adsorbent comprises an ion-exchanged zeolite selected from the group consisting of zeolite X, zeolite Y, zeolite LSX, and mixtures thereof, the zeolite having exchangeable cationic sites, and
10 at least some, perhaps a majority, of the sites have silver cation or copper cation present. In one preferred embodiment, the majority of the cationic sites of the ion-exchanged zeolite contain silver cation. In another preferred embodiment, essentially all cationic sites of the ion-exchanged zeolite contain the silver cation.

Without being bound to any theory, it is believed that the preferential
15 adsorption occurs by π -complexation.

In a preferred embodiment, the diene is selected from the group consisting of butadiene, hexadiene, octadiene and mixtures thereof. In an exemplary embodiment, the diene is 1,3-butadiene, and the mixture includes 1,3-butadiene and at least one other C₄ unsaturated compound. In a further exemplary embodiment, the
20 mixture comprises at least one mono-olefin having as many carbon atoms as the diene, the diene is selected from the group consisting of butadiene, hexadiene, octadiene, and mixtures thereof; and the mono-olefin is selected from the group consisting of butene, hexene, octene, and mixtures thereof. In an exemplary example, the mono-olefin is butene and the diene is butadiene. The mono-olefin may
25 be in a gaseous state and saturated with the diene.

The method may further comprise the step of changing at least one of the pressure and temperature to thereby release the diene-rich component from the adsorbent. In a preferred embodiment, the selected pressure of preferential
adsorption is a first pressure, and the pressure of release is a second pressure less than
30 the first pressure. In a more preferred embodiment, the first pressure is in a range of

about 1 atmosphere to about 35 atmospheres, and the second pressure is in a range of about 0.01 atmosphere to about 5 atmospheres. Further, the selected temperature of preferential adsorption is a first temperature, and the temperature of release is a second temperature greater than the first temperature. In a preferred embodiment, the first temperature is in a range of about 0°C to about 150°C, and the second temperature is in a range of about 70°C to about 250°C.

This adsorbent also fortuitously and unexpectedly substantially maintains its adsorbent capacity and preference for the diene in the presence of the sulfur compound.

In an alternate embodiment, a method is disclosed for separating a diene from a mixture including the diene and a sulfur compound. In an exemplary embodiment, the diene is selected from the group consisting of butadiene, hexadiene, octadiene, and mixtures thereof. The process comprises the step of contacting the mixture with an adsorbent which preferentially adsorbs the diene at a first temperature, thereby producing a non-adsorbed component and a diene-rich adsorbed component. The adsorbent comprises zeolite A having exchangeable cationic sites, a plurality of the zeolite A sites having an alkali metal cation or an alkaline earth metal cation present.

The method may further comprise the step of releasing the diene-rich adsorbed component from the adsorbent by elevating the temperature to a second temperature which ranges between about 70°C and about 120°C.

In a preferred embodiment, a selected pressure of preferential adsorption is a first pressure, and a pressure of release is a second pressure less than the first pressure, wherein the first pressure is in a range of about 1 atmosphere to about 35 atmospheres, and the second pressure is in a range of about 0.01 atmosphere to about 5 atmospheres.

This adsorbent also fortuitously and unexpectedly substantially maintains its adsorbent capacity and preference for the diene in the presence of the sulfur compound.

As demonstrated below, the sulfur compound is generally hydrogen sulfide. The novel adsorbents were exposed to very severe amounts, for example the hydrogen sulfide was present in amounts up to about 66 mole%. In sharp contrast, a conventional cracked gas stream before any desulfurizing distillation steps contains hydrogen sulfide present in amounts of about 0.01 mole%. As such, the data presented hereinbelow indicate that the novel adsorbents of the present invention would be quite robust, ie. very tolerant and/or resistant to H₂S under normal operating conditions.

To further illustrate the present invention, the following examples are given. It is to be understood that these examples are provided for illustrative purposes and are not to be construed as limiting the scope of the present invention.

EXAMPLES

Effect of sulfur compounds on olefin selective sorbents

In order to study the effect of sulfur compounds on the AgNO₃/SiO₂ sorbent, Hydrogen Sulfide (H₂S) was used as a model compound. Several isotherms of H₂S were measured at 70°C over AgNO₃/SiO₂ and SiO₂ sorbents and are shown in Figure 1. H₂S adsorption on AgNO₃/SiO₂ was mostly reversible with only about 0.04 mmol/g of H₂S left on the surface. The effect of H₂S on olefin adsorption on AgNO₃/SiO₂ can be observed in Figure 2. After the sorbent was exposed to 1 atm of H₂S at 70°C, C₃H₆ capacity at 1 atm and 70°C was reduced from 1.6 to 1.5 mmol/g. This constituted a 6% reduction in C₃H₆ capacity. While it seems that the sorbent is affected negatively by the presence of H₂S, its effects were not as harmful as expected. Therefore, minimal or accidental exposure to sulfur compounds would not result in the total loss of the adsorption bed.

Silica gel is a very good sorbent for both olefins and paraffins, but it does not have selectivity (about 1.1) for one as opposed to the other. In the presence of H₂S, it can be seen that the inventive sorbent(s) have about the same selectivity as they had before exposure to H₂S. One can conclude from this that the hydrocarbons are fortuitously adsorbing even on sulfur covered surfaces.

In the following cycling studies many ethylene and propylene adsorption cycles were run on $\text{AgNO}_3/\text{SiO}_2$. There was virtually no capacity loss below 50°C . $\text{AgNO}_3/\text{SiO}_2$ has been demonstrated to be very stable, and this is a highly favorable aspect of the adsorbent.

5 Cycling Studies

These are simply many adsorption experiments repeated continuously using the same adsorbent. The data correspond to 80 cycles of 20 minutes each. A straight, horizontal line on the plot means that the equilibrium loading is the same for every cycle. This suggests that the Ag^+ remains fully active on the adsorbent throughout the service life. The 50°C graphs (Figures 3 and 4) for C_2H_4 and C_3H_6 are not exactly horizontal, although they do show a consistent loading range throughout many cycles.

The 120°C data (Figure 5) for C_3H_6 however, shows that loading begins to decrease sharply initially, and then to a new plateau. The loss of capacity likely suggests that some of the Ag^+ sites are somehow losing activity. High temperatures usually accelerate the rate of degradation for all adsorbents in general.

15 H_2S Adsorption/Desorption on $\text{AgNO}_3/\text{SiO}_2$

C_3H_6 has been shown to be readsorbed at 70°C onto a $\text{AgNO}_3/\text{SiO}_2$ adsorbent that was previously exposed to 1 atm of H_2S . As shown in the earlier graphs, it appears that a substantial portion of the H_2S desorbs upon lowering the pressure. See Figures 6-8. The "poisoned" adsorbent thus refers to adsorbent containing residual H_2S that is adsorbed irreversibly. From the C_3H_6 data (Figure 9), we see that the capacity has diminished only slightly.

Sorbent for purification of 1-Hexene by removal of benzene

25 See Figure 15.

Effects of H_2S on AgY zeolite for 1,3-Butadiene/1-Butene Adsorption

Some H_2S is adsorbed on Ag-Y irreversibly. However, purification capability of Ag-Y was maintained by shifting the adsorption of both adsorbates to higher pressure. See Figures 10-14.

Purification of butene by removal of trace amounts of butadiene was successfully achieved at Chevron by using Ag ion-exchanged zeolite (Ag-Y). In an actual purification process, certain amounts of H₂S and H₂ may be present in the process stream. In this report, the effect of H₂S exposure on butadiene/butene adsorption will be examined.

Experimental

Ag-Y (Si/Al=2.43) was prepared by the ion exchange of Na-Y (Si/Al=2.43, Strem Chemical) in excess amounts of Ag cations. First the gas phase adsorption isotherms of H₂S were measured at 25 - 180°C using a gravimetric method (SHIMADZU TGA-50) in order to understand the reversibility of H₂S adsorption on Ag-Y. Then, isotherms of 1,3-butadiene and 1-butene on Ag-Y were examined before and after H₂S exposure. The sorbent was subjected to H₂S exposure at 0.66 atm for 10 minutes at either room temperature or 120°C, which is extremely severe compared to the actual level of H₂S present in the process stream, so that the effect on the sorbent after long time usage can be understood.

Results and Discussion

Adsorption and desorption isotherms of H₂S on Ag-Y at 25°C, 70°C and 120°C are shown in Figure 16. It was found that H₂S was irreversibly adsorbed on Ag-Y at lower pressure ranges less than 0.2 atm. Also, a fairly large amount of H₂S was adsorbed on Ag-Y even at a low pressure of 7x10⁻⁴ atm. At 180°C (not shown here), the weight of Ag-Y in the TGA-50 increased continuously in the presence of H₂S. These results indicate a reaction between Ag-Y and H₂S occurred at 180°C and even at lower temperatures such as 25 - 120°C. One possible reaction is the formation of Ag₂S. Actually, the color of Ag-Y changed from white to dark brown, which is the color of Ag₂S. Analytical investigation such as XPS (X-ray Photoelectron Spectroscopy) would be helpful to understand the reaction products.

Adsorption isotherms of 1,3-butadiene and 1-butene are plotted in Figure 17, compared with isotherms of the adsorbates for the novel adsorbents having not been exposed to H₂S (labelled "Joel et al."). Isotherms of both adsorbates in the present invention have a lower threshold pressure than those labelled "Joel et

al." The threshold pressure is the value where the steep rise in the isotherm occurs. At present, the reason for this difference is not clear except the sample preparation conditions were slightly different. However, based on the results in Fig. 17, the sorbent in this work is also useful for purification of butene by removal of butadiene and was used for further studies on the H₂S effect.

The effect of H₂S on adsorption isotherms of butadiene and butene are examined in Figures 18 and 19, respectively. Irreversible H₂S adsorption amounts after H₂S exposure are indicated in the figures. In both cases, adsorption amounts at the same partial pressure were decreased. And the partial pressures of adsorbates for the same adsorption amounts were shifted to higher pressures by H₂S exposure. However, it was clearly demonstrated that Ag-Y sorbent maintained its purification capability even after this severe H₂S exposure test as shown in Figure 20, which compares isotherms of Ag-Y containing 2.0-2.3 mmol/g of irreversibly adsorbed H₂S.

Although some H₂S appeared to be irreversibly adsorbed on Ag-Y, purification capability of Ag-Y was maintained by shifting the adsorption of both adsorbates to higher pressures.

In conclusion, as stated above, H₂S is always present to some extent in cracked gas streams. It is typically removed with conventional technology prior to the olefin-paraffin separation step. In the case of Ag⁺-based systems (eg. the classical, aqueous AgNO₃ adsorption systems), the presence of H₂S leads to loss of silver ions through the formation of silver sulfide, Ag₂S. The reaction between H₂S and Ag⁺ ions in water is known to occur very readily. The Ag₂S formed is a finely-divided precipitate that is highly insoluble in water. The room temperature solubility of AgNO₃ in water is 216 g/L, while that of Ag₂S is 1.4 X 10⁻⁴ g/L. For solid adsorbents containing monodispersed or ion-exchanged Ag⁺, one would expect a similar sulfide-forming reaction to occur with H₂S. That is, some or all of the Ag⁺ will likely "come off" of the adsorbent as Ag₂S particles. The effectiveness of the adsorbent for olefins should therefore be greatly reduced.

The present inventive findings are unexpected and remarkable in this regard. From the collected data, there is evidence that some H₂S adsorbs irreversibly onto AgY and AgNO₃/SiO₂. However, it appears that the adsorbents still have sufficient capacity and selectivity for olefins over paraffins. Without being bound to
5 any theory, it is believed that the reason for this may be that the silver in the "poisoned" Ag₂S sites are sufficiently "ionic" so that they are in the +1 state, and thus able to pi-complex with olefins.

Detailed Description of the sulfur resistant adsorbents

The invention provides novel sulfur resistant adsorbents for use in a
10 method of separating selected gaseous hydrocarbons from a gaseous mixture comprising such hydrocarbons. The adsorbents are particularly suited for selective adsorption of alkenes such as ethylene, propylene, and mixtures of these from a gaseous mixture comprising alkenes. In one embodiment, the method comprises first
15 contacting the gaseous mixture with an adsorbent comprising a metal compound which preferentially adsorbs the alkene, at a selected temperature and pressure, thereby producing a non-adsorbed component and an alkene-rich adsorbed component. The adsorbent comprises a metal compound, preferably a silver or copper compound supported on a carrier. The preferred carrier comprises a plurality of pores having size greater than the effective molecular diameter of the alkene. The
20 compound of silver or copper is characterized by formation of π -complexation bonds between the silver or copper and the alkene for releasably retaining the alkene. Then the pressure and/or temperature are changed to thereby release the alkene-rich component from the adsorbent.

The metal compound is preferably a salt selected from acetate,
25 benzoate, bromate, chlorate, perchlorate, chlorite, citrate, nitrate, nitrite, sulfate, halide (F, Cl, Br, I), and mixtures of these. The carrier is a high surface area support selected from refractory inorganic oxide, molecular sieve, and activated carbon, and mixtures of these. The preferred metal is selected from silver and copper, and mixtures thereof.

In one embodiment, the adsorbent is characterized by preferential adsorption of gaseous alkene from a gaseous mixture comprising the alkene, and the adsorbent comprises: a salt of silver supported on a carrier. The preferred salt is silver nitrate. Other salts of silver are as per the group defined above, where the preferred halide is fluoride.

Preferably, the adsorbent comprises finely divided particles of silica (SiO_2) with silver nitrate dispersed on and supported on the particles.

Another preferred adsorbent is a salt of copper selected from the group consisting of bromide, fluoride, iodide and sulfate, supported on a carrier.

The carriers are refractory inorganic oxide, molecular sieve, and activated carbon, are preferably characterized by a BET surface area greater than about 50 square meters per gram and up to about 2,000 square meters per gram and comprise a plurality of pores having size greater than about 3 angstroms and up to about 10 microns.

In a preferred embodiment, the metal compound retains its chemical characteristic. Therefore, dispersion onto a carrier is preferably conducted under conditions that do not decompose or oxidize the metal compound. In addition, the preferred metal compound is one that provides the metal in a +1 oxidation state. The preferred dispersion method leads to such preferred +1 valance state. Preferably, the metal compound is water soluble to facilitate dispersion, particularly by incipient wetness technique. Therefore, the preferred compound contains Ag(I) or Cu(I) cationic species with associated anionic species, as per the compound and salts listed above. As a result, these π -complexation adsorbents of the invention provide attractive and improved results compared to conventional adsorbents.

Separation by π -complexation is a subgroup of chemical complexation where the mixture is contacted with a second phase, which contains a complexing agent. The advantage of chemical complexation is that the bonds formed are stronger than those by van der Waals forces alone, so it is possible to achieve high selectivity and high capacity for the component to be bound. At the same time,

the bonds are still weak enough to be broken by using simple engineering operations such as raising the temperature or decreasing the pressure.

The further description and examples below show that for C_3H_6/C_3H_8 separation, conventional sorbents did not provide a large working capacity for C_3H_6 since the C_3H_6 isotherms do not exhibit a steep portion between adsorption and desorption pressures. The examples also show that the sorbents of the invention have superior selectivity for C_3H_6 adsorption. The examples show use of the new adsorbents (sorbents) with a preferred PSA process for very effective gas separation.

The PSA process is effectively usable with the new sorbents of the invention. Here, multiplicity of periodic steady states is an important aspect of cyclic adsorption process. For pressure swing adsorption (PSA), multiple steady states exist for a fixed set of operating conditions, over a particular range of one or more of these operating variables (i.e., bifurcation variables). The final stable state depends only on the initial condition (i.e., the perturbation variables). Such an example of multiplicity in PSA has been presented for the system of $H_2S/CO_2/CH_4$ on 5A zeolite. Efficient methods for direct determination of periodic steady states as well as mapping regions with different bifurcation diagrams are applied to PSA. Here, there is used a region of multiplicity for C_3H_6/C_3H_8 separation by PSA coupled with the new sorbents.

FURTHER EXAMPLES

Example 1

$AgNO_3$ Supported on SiO_2 Prepared by Thermal Monolayer Dispersion and Incipient Wetness Impregnation

The sorbents of the invention are metal compounds which contain metal cations dispersed over a high surface area substrate. The dispersion of metal compounds and their included cations was accomplished using several methods. This was done to determine which technique was better suited for preparing π -complexation sorbents. One of the methods is known as spontaneous thermal monolayer dispersion. The other technique utilized was incipient wetness

impregnation. Here, these techniques were applied to synthesize sorbents capable of π -complexation with olefins.

Thermal monolayer dispersion involves mixing a metal compound, preferably a metal salt, with a substrate at a predetermined ratio. This ratio is
5 determined by the amount of salt that is required for monolayer coverage on the surface area of the substrate assuming two-dimensional close-packing. The BET surface area of the substrate was first measured. After the finely divided powders of the salt and substrate have been thoroughly mixed, it was heated at a temperature between the Tammann temperature and the melting point of the salt. If the
10 temperature was too low, the dispersion would take an unacceptably long time. However, a high dispersion temperature could cause the metal salt to oxidize or react with the substrate, both of which could deactivate the sorbent. The sorbent in the example was prepared by mixing 0.32 grams of AgNO_3 (Strem Chemicals) per gram of SiO_2 (Strem Chemicals). After thorough mixing, the sample was heated in air at
15 200°C for 89 hours to assure complete dispersion. This sorbent is referred to as monolayer $\text{AgNO}_3/\text{SiO}_2$. The BET surface area of this sample was measured at $384\text{ m}^2/\text{g}$. The above ratio yielded the best results for this dispersion technique.

Another technique utilized was incipient wetness impregnation. It involved preparing a solution of the salt to be dispersed. The solution was then
20 mixed with the substrate where it was absorbed by the substrate due to incipient wetness. After the substrate had imbibed the solution containing the salt into its pore structure, the sample was heated to remove the solvent. Care needs to be taken when selecting solvents for use in this technique. Firstly, the salt needs to be soluble in the solvent to a sufficient extent so as to allow enough salt to be dissolved in the volume
25 of solution that is equal to the pore volume of the substrate. Secondly, the solvent selected needs to be able to wet the surface of the substrate. As mentioned above, $\text{AgNO}_3/\text{SiO}_2$ at a ratio of 0.32 was the sorbent utilized. Since AgNO_3 is highly soluble in water, water was chosen as the solvent. Also, since SiO_2 has a high affinity for water, this also assures proper wetting of the substrate. The pore volume
30 and surface area of the SiO_2 utilized were measured at $0.46\text{ cm}^3/\text{g}$ and $670\text{ m}^2/\text{g}$,

respectively. A 1.2 M solution of AgNO_3 was prepared. A volume of the solution equal to the total pore volume of SiO_2 sample was brought in contact with the substrate, so that a $\text{AgNO}_3/\text{SiO}_2$ ratio equal or close to 0.32 was achieved. The sample was then heated for 4 hours at 105°C in air to remove the water. The ratio of the resulting sample was calculated at 0.27 and the sample was used without further treatment. The BET surface area of this sorbent was $398\text{ m}^2/\text{g}$. The sorbent prepared by incipient wetness impregnation is referred to as impregnated $\text{AgNO}_3/\text{SiO}_2$. The loadings of AgNO_3 on the samples were optimized by maximizing olefin adsorption while varying the salt content.

10 Adsorbates

The hydrocarbons used as the adsorbates were ethane (CP grade, Matheson minimum purity 99.0%), ethylene (CP grade, Matheson minimum purity 99.5%), propane (CP grade, Matheson minimum purity 99.0%), propylene (CP grade, Matheson minimum purity 99.0%), and helium (pre-purified grade, Metro Welding 99.995%) was used as the carrier gas and as the regeneration gas. The gases were used without further purification.

Measurements of Equilibrium Isotherms and Uptake Rates

Isotherms and uptake rates were measured utilizing both a Shimadzu TGA-50 microbalance and a Micromeritics ASAP 2010 system following the procedures described in Ackley and Yang (1991). Equilibrium time for isotherm measurements was about 5 minutes per equilibration point. Surface area measurements were made using the Micromeritics ASAP 2010. Also, measurements were made at two temperatures (25°C , 70°C) in order to obtain isosteric heats of adsorption. The overall diffusion time constants, D/R^2 , were calculated from the uptake curves measured from a stepped pressure increment from 0 to 0.1 atm by methods and assumptions described in detail in Yeh (1989).

Equilibrium Isotherm Model

Since the adsorption of paraffin molecules includes physical adsorption only, it can be modeled well by the Langmuir isotherm with two parameters shown in equation A.

However, the adsorption of olefin molecules on $\text{AgNO}_3/\text{SiO}_2$ includes both physical adsorption and chemisorption (via π -complexation). Therefore, a different model is required to account for chemisorption. The isotherm model developed by Yang and Kikkinides (1995) to account for both interactions is shown in equation B.

The first term accounts for physical adsorption, while the second term represents contributions by chemisorption. The second term also takes into account the energetic heterogeneity of the surface ion sites available for complexation. While equation B contains five parameters, only two of them are true fitting parameters (Yang and Kikkinides, 1995). The other three parameters have certain constraints imposed on them in order for them to have physical meaning. Empirical values for s are available from the literature (Valenzuela and Myers, 1989; Kapoor and Yang, 1990). For each adsorbent, the corresponding paraffin data were used first to obtain the two parameters in the Langmuir isotherm. Therefore, equation B was used to fit the olefin adsorption data with imposed values or constraints on q_{mp} and b_{p} , and s , leaving only q_{mc} and b_{c} as true fitting parameters.

Thermal Monolayer Dispersion vs. Incipient Wetness Impregnation for Preparing AgNO_3 Supported on SiO_2

As mentioned earlier, the thermal dispersion involves heating a mixture of metal salt and substrate. This could lead to oxidation or partial oxidation of the metal salt, which would reduce the complexation with olefin molecules. It was determined that FeCl_2 could be easily oxidized to FeCl_3 during the thermal monolayer dispersion process. As also described earlier, metal cations can be spread by incipient wetness impregnation. Sorbents prepared by these two techniques are compared in this example. It should be noted that thermal monolayer dispersion (TMD) is also referred to as thermal dispersion. These terms are used

interchangeably throughout this description. It should be noted that the incipient wetness impregnation method also results in the creation of a monomolecular layer or monolayer of the salt dispersed on the carrier or support. Therefore, as used herein, impregnation refers to the monolayer achieved by the more superior incipient wetness method and thermal dispersion generally refers to application of the salt onto an adsorbent by high temperature thermal processing.

AgNO₃/SiO₂ sorbent capable of π -complexation was prepared via thermal monolayer dispersion. The procedure for the preparation of the sorbent was described in the previous section, including that the process was carried out at 200°C for 89 hours in order to allow sufficient time for the dispersion of the AgNO₃ salt. The resulting sorbent had a light gray color which suggested that some of the AgNO₃ had been oxidized during the process. The BET surface area of the sorbent was measured at 384 m²/g. The average pore diameter of the sorbent was calculated using the Horvath-Kawazoe method to be 8.4Å.

Equilibrium isotherms of C₂H₄ and C₂H₆ on SiO₂ (substrate) and monolayer AgNO₃/SiO₂ (by thermal dispersion) at 70°C are shown in Figure 21. The equilibrium data for C₂H₆ and C₂H₄ were fitted to equations A and B, respectively. Fitting parameters for these isotherms are shown in Table A. Although both gases adsorbed similar amounts on the SiO₂ surface, the adsorbed amount of C₂H₄ was slightly higher than that for C₂H₆. From Figure 21, it can be seen that the bare surface of SiO₂ showed no substantial selectivity. The selective adsorption ratio of C₂H₄ over C₂H₆ for SiO₂ was approximately 1.5. The preference toward C₂H₄ is due to higher polarizability. This allows C₂H₄ to better interact with the electric field on the surface of the SiO₂ substrate. Compared to SiO₂, monolayer AgNO₃/SiO₂ demonstrated a substantial increase in selectivity and capacity for olefin. The selective adsorption ratio of C₂H₄ over C₂H₆ was increased from 1.5 to 4. On monolayer AgNO₃/SiO₂ at 70°C and 1 atm, the amount adsorbed for C₂H₄ was 0.5 mmol/g. It appears that the increase in C₂H₄ adsorption on monolayer AgNO₃/SiO₂ was not large when compared to adsorption on bare SiO₂. However, it becomes more

significant when one compares the amounts adsorbed per surface area. The amount of C_2H_4 adsorbed per surface area increased two fold on $AgNO_3/SiO_2$.

In order to compare thermal monolayer dispersion with incipient wetness impregnation, equilibrium isotherms for C_2H_4 and C_2H_6 at $70^\circ C$ on wet
5 impregnated $AgNO_3/SiO_2$ are shown in Figure 22. The equilibrium data for C_2H_6 and C_2H_4 was fitted with equations A and B, respectively. The fitting parameters are shown in Table A. When compared with the sorbent synthesized by thermal monolayer dispersion, this sorbent showed superior capacity and a higher selectivity. At 1 atm and $70^\circ C$, on impregnated $AgNO_3/SiO_2$, the amount adsorbed of C_2H_4 was
10 1.25 mmol/g. The capacity of this sample was 2.5 times greater than that on the same sorbent prepared by thermal monolayer dispersion. The selective adsorption ratio was 6.5. This was approximately a 60% increase over monolayer $AgNO_3/SiO_2$. Both sorbents demonstrated completely reversible adsorption behavior.

Figure 22A shows equilibrium isotherms of C_2H_4 and C_2H_6 at $25^\circ C$
15 on $AgNO_3/SiO_2$ sorbent. This sorbent was prepared by impregnating SiO_2 with the $AgNO_3$, using incipient wetness technique to achieve a monomolecular layer of the Ag salt on the SiO_2 carrier. Comparing Figures 21 and 22A, there is shown significant improved performance of the impregnated (incipient wetness prepared) $AgNO_3$ on SiO_2 sorbent as compared to the thermally dispersed $AgNO_3$ on SiO_2 . The
20 impregnated sorbent (Figure 22A) has a shape of the isotherm that is higher above the knee. This isotherm shape is desirable because it increases the working capacity of the sorbent. Comparing Figures 21 (thermally dispersed) and 22A (impregnated) it is clear that the impregnated sorbents are superior.

The enhanced performance of the impregnated sorbents (Figures 22
25 and 22A) over the thermally dispersed sorbents (Figure 21) is clear. The amounts of C_2H_4 adsorbed in Figures 22 and 22A are far greater at each partial pressure than the amount adsorbed in Figure 21 at the same respective partial pressure.

One possible explanation for the increased adsorption capacity of the sorbent prepared via wet impregnation was better salt dispersion and hence less pore
30 blockage. However, when the surface areas were compared (380 vs. 389 m^2/g), no

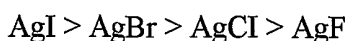
significant differences were encountered. Also, the fact that diffusion in both samples was fast indicated no or minimal pore blockage. Complete diffusional uptake was achieved in less than 90 seconds for both sorbents. Another possible explanation was the AgNO_3 loading on the sample. Again when both loadings were compared (0.32 vs. 0.27), no significant difference was encountered that accounts for the large difference on adsorption capacities. Lastly, the only plausible explanation for the discrepancies was the nature or oxidation states of the dispersed cations. As mentioned, thermal monolayer dispersion could lead to partial oxidation of the salt. Since AgNO_3 was exposed to air at 200°C for 89 hours during thermal monolayer dispersion, it is possible that some of the salt was oxidized to some extent. A simple evidence for partial oxidation and decomposition was the observation of the color of the resulting sample which had a light gray color with some black particles. This observation indicated that some of the AgNO_3 salt (which is colorless) was decomposed and oxidized to Ag_2O and AgO (gray and black, respectively). The decomposition/partial oxidation of some of the AgNO_3 would certainly decrease the complexation with olefin and hence the adsorption capacity.

Example 2

Anion Effects - Ag-Halide Compounds Supported on SiO_2

In this example, the effect of various anions on olefin adsorption are shown. By understanding this effect, the adsorptive properties of sorbents are maximized for olefin/paraffin separation. The sorbents were prepared by dispersing silver halides on silica gel via thermal monolayer dispersion. Incipient wetness impregnation was not used due to lack of good solvents. The halides used were AgF , AgCl , AgBr , AgI . The silver halide content of each sorbent was maintained at around 1.0 mmol/g to facilitate comparison. The sorbents were prepared by mixing the metal halide and the silica gel with thorough mixing. The resulting mixture was heated in air at 350°C for 4 days to assure proper spreading. The BET surface areas of the resulting sorbents are shown in Table B.

Equilibrium isotherms for C_3H_6 at $25^\circ C$ on the various AgX/SiO_2 (where $X=F, Cl, Br, \text{ or } I$) sorbents are shown in Figure 23. The fitting parameters for these isotherms are shown in Table C. The amounts of C_3H_6 adsorbed at 1 atm for $AgF, AgCl, AgBr$ and AgI on SiO_2 were 1.44, 1.34, 1.51, and 1.47 mmol/g, respectively. All isotherms were fully reversible. Initially, it would appear that anions have very slight effect. However, when the data are normalized to account for differences in surface area, a clear trend emerged. The normalized data are shown in Figure 24. The weakly chemisorbed C_3H_6 on the surface metal cations can be represented by the following formula: $Ag^+(C_3H_6)_n$. The values of n for $AgF/SiO_2, AgCl/SiO_2, AgBr/SiO_2, AgI/SiO_2$ at 1 atm and $25^\circ C$ were 0.10, 0.13, 0.16 and 0.23 molecule C_3H_6 per Ag^+ . Therefore, once the data was normalized, the adsorption trend was observed as follows:



The above trend is also supported by isosteric heat of adsorption data obtained from the temperature dependence of the equilibrium isotherms. Isosteric heat of adsorption ($-\Delta H$) values for propylene on $AgF/SiO_2, AgCl/SiO_2, AgBr/SiO_2$ and AgI/SiO_2 were 7.6, 8.2, 9.0, and 9.9 kcal/mol, respectively.

The π -complexation bond involves σ -donation (i.e., overlap of the 2p orbital of olefin with the 5s orbital of Ag^+) and $d-\pi^*$ backdonation (i.e., electron donation from the $4d_{yz}$ orbital of Ag^+ to the $2p^*$ orbital of olefin). For anions with higher electronegativities (e.g., F^-), the σ -donation is stronger. However, the $d-\pi^*$ backdonation dominates the bonding in this case, and the backdonation follows the order shown above.

Example 3

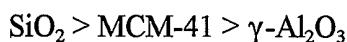
Substrate Effects - $AgNO_3$ Supported on $\lambda Al_2O_3, SiO_2$ and Zeolite

In order to gain a better understanding of the behavior of π -complexation sorbents, it is necessary to also understand the effects of various substrates on olefin adsorption. This example shows the effect that the chemical and structural properties of the substrate had on adsorption behavior. To this end, several

sorbents were prepared by dispersing AgNO_3 over three different high surface area substrates using the incipient wetness impregnation technique described previously. The substrates used were $\gamma\text{-Al}_2\text{O}_3$, SiO_2 and MCM-41 mesoporous zeolite. The MCM-41 utilized is one of a new family of mesoporous silicate molecular sieves with hexagonal arrangement of unidimensional channels with uniform sizes in the range of 20-100 Å (Kresge, et al., 1992; Beck et al., 1992). The MCM-41 utilized had a BET surface area of 1004 m^2/g and an average pore size measured by the Horvath Kawazoe method to be 30 Å. The $\gamma\text{-Al}_2\text{O}_3$ utilized was obtained from Alcoa (PSD-350) and had a BET surface area of 340 m^2/g . The metal salt loading per surface area was maintained constant for each sorbent. The AgNO_3 loadings for $\gamma\text{-Al}_2\text{O}_3$, SiO_2 , and MCM-41 were 0.16, 0.27 and 0.47 gram of salt per gram of substrate, respectively.

Equilibrium isotherms for C_3H_6 on wet impregnated $\text{AgNO}_3/\gamma\text{-Al}_2\text{O}_3$, $\text{AgNO}_3/\text{SiO}_2$ and $\text{AgNO}_3/\text{MCM-41}$ at 70°C are shown in Figure 25. The fitting parameters for these isotherms are shown in Table D. Adsorption capacities at 1 atm and 70°C for $\text{AgNO}_3/\gamma\text{-Al}_2\text{O}_3$, $\text{AgNO}_3/\text{SiO}_2$ and $\text{AgNO}_3/\text{MCM-41}$ were 0.48, 1.49, and 2.06 mmol/g, respectively. C_3H_6 adsorption on these sorbents was completely reversible. As shown in Figure 25, all isotherms showed good working capacities which are crucial for pressure swing adsorption process (PSA). Uptake rates on all sorbents were fast with completion within 300 seconds. The overall diffusion time constants (D/R^2), surface areas and average pore diameters for $\text{AgNO}_3/\gamma\text{-Al}_2\text{O}_3$, $\text{AgNO}_3/\text{SiO}_2$ and $\text{AgNO}_3/\text{MCM-41}$ are shown in Table E. Selective olefin over paraffin adsorption is shown in Figure 26 for C_3H_6 and C_3H_8 at 25°C on wet impregnated $\text{AgNO}_3/\text{SiO}_2$. The selective adsorption ratio of this sorbent at 1 atm was 6. The working capacity of a sorbent is determined by the isotherm's steepness above the knee. In order to clearly show the effect of the chemical properties of the sorbent's surface rather than the physical properties (surface area, pore size), the data was normalized to prevent bias toward the samples with higher surface areas. The normalized equilibrium data for the C_3H_6 adsorption at 70°C on $\text{AgNO}_3/\gamma\text{-Al}_2\text{O}_3$,

AgNO₃/SiO₂ and AgNO₃/MCM-41 are shown in Figure 27. Once the data had been normalized the following trend for the substrates is observed:

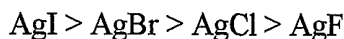


The surfaces of SiO₂ and Al₂O₃ are both filled with oxygen atoms.

5 Pure SiO₂ surface has no acidity, whereas Al₂O₃ has acidity due to oxide vacancies. Consequently, there are more Ag⁺ ions that are 4-coordinated on the SiO₂ surface as compared to the Al₂O₃ surface, and there are more 5- and 6- coordinated Ag⁺ on the Al₂O₃ surface. It is more favorable for the 4- coordinated Ag⁺ ions to bond C₂H₄ molecules. The 5- and 6- coordinated Ag⁺ ions are unlikely to bond olefins due to
10 stereochemical reasons. The experimental results indeed showed that SiO₂ is significantly better as a substrate.

Examples 1 to 3 show new and more effective sorbents for ethane\ethylene and propane\propylene separations were synthesized by dispersing AgNO₃ salt over several substrates (γ-Al₂O₃, SiO₂ and MCM-41) using incipient
15 wetness impregnation technique. The capacities and selectivities of these new sorbents are significantly better than any known π-complexation sorbents. Adsorption rates for these sorbents were fast with 100% completion achieved within 300 seconds at 25°C. These characteristics make the sorbents most promising for use with pressure swing adsorption processes (PSA) which is described in the
20 examples which follow later (Yang, 1987).

It was demonstrated that anions have significant effects on the adsorption behavior of π-complexation sorbents. It was shown that the anion effects on the selective olefin adsorption followed the trend described below:



25 This trend is opposite to the electronegativities of the anions. This was because the d-π* backdonation, rather than the σ-donation, dominated the bonding between olefin and Ag⁺.

One of the objectives was to determine the effect various substrates have on selective olefin adsorption based on π-complexation. While the effect of the
30 physical characteristics of a substrate such as a surface area and pore size would have

on adsorption is clear, the effect of the surface chemistry properties (i.e., lyophobicity, hydrophobicity, etc.) is not well understood. The substrates selected were γ - Al_2O_3 , SiO_2 , and MCM-41. Once the data was normalized to take into account surface area, the following trend was observed:

5
$$\text{SiO}_2 > \text{MCM-41} > \gamma\text{-Al}_2\text{O}_3$$

The silica surface (on both silica gel and MCM-41) provides a better substrate due to the lack of surface oxide vacancies (unlike γ - Al_2O_3), and consequently there are more four-coordinated Ag^+ (which can bond olefin) and less 5- and 6-coordinated Ag^+ (which cannot bond olefin for steric reasons).

10 From the results presented in examples 1 to 3, it is clear that anions and substrate play an important role in selective olefin adsorption via π -complexation. It is possible to use these differences to manipulate the adsorptive properties of sorbents to better suit a particular application, such as PSA described below.

15 **Example 4 - PSA Cycle Using $\text{AgNO}_3/\text{SiO}_2$ and Comparative Adsorbents**

The effectiveness of these silver salt compounds was further compared to other adsorbents. Three sorbents were used in the following examples; two were commercial sorbents, (4A zeolite and carbon molecular sieve) and one was a π -complexation sorbent of the invention described above ($\text{AgNO}_3/\text{SiO}_2$). The
20 comparison was based on modelling a PSA cycle, representative of a commercial use of such adsorbents. Equilibrium isotherms, heats of adsorption, and temperature-dependent diffusivities were measured for four gases on three sorbents.

The 4A-type zeolite used was in powder form. The samples were degassed *in vacuo* (10^{-6} torr) at 350°C before each experiment. The carbon
25 molecular sieve (CMS) utilized in this work was manufactured by Bergbau-Forschung GmbH in Germany. Unlike Type-4A zeolite, which has a discrete pore size, Bergbau-Forschung CMS has a pore-size distribution between 3 and 5 Å. The sample utilized in this work was in pellet form. The pelletized form of CMS does not affect diffusion measurements, since diffusion processes in Bergbau-Forschung

CMS are controlled by intracrystalline diffusion. The CMS samples were degassed *in vacuo* at 90°C before each experiment.

The π -complexation sorbent used in this work was prepared using thermal monolayer dispersion to disperse AgNO_3 over an SiO_2 substrate. The sorbent was prepared by mixing 0.32 of AgNO_3 (Stem Chemicals) per gram of SiO_2 (Stem Chemicals). The SiO_2 had a surface area of 670 m^2/g and a pore volume of 0.46 cm^3/g . The particle size of the SiO_2 utilized ranged from 100 to 200 mesh. After thorough mixing, the sample was heated in air at 200°C for 89 h to assure complete dispersion. The BET surface area of the sorbent was measured at 384 m^2/g by nitrogen adsorption at 77 K. Pore size was calculated to be 23 Å using the BJH method described in detail by Barrett, et al. (1951). Other $\text{AgNO}_3/\text{SiO}_2$ ratios were also used; the ratio just given yielded the best results.

Equilibrium isotherms, uptake curves, and surface-area measurements were made utilizing a Micromeritics ASAP 2010 adsorption instrument and a Shimadzu TGA-50 thermogravimetric analyzer. The ASAP 2010 utilizes a volumetric system to obtain adsorption isotherms and uptake curves. All uptake curves were measured at a stepped pressure increment from 0 atm to 0.1 atm. Also measurements were made at various temperatures to obtain isosteric heat of adsorption data and the temperature dependence of diffusivities. Surface-area measurements were carried out by nitrogen adsorption at 77 K. The hydrocarbons used were: ethane (CP grade, Matheson minimum purity 99.0%), ethylene (CP grade, Matheson minimum purity 99.5%), propane (CP grade, Matheson minimum purity 99.0%), propylene (CP grade, Matheson minimum purity 99.0%). The gases were used without further purification.

25 Description of the PSA Cycle

A four-step PSA cycle similar to that used by Kikkinides et al. (1993) was used in all the cases in this example. The steps involved with each cycle were as follows: (1) pressurization with the feed gas (mixture of 50% olefin and 50% paraffin on molar basis); (2) high-pressure adsorption with feed gas, that is, feedstep; (3)

high-pressure cocurrent purge with part of the olefin-rich product obtained in step (4); (4) countercurrent blowdown to a low pressure. All steps were of equal time duration.

Figure 28 shows the PSA cycle used. As can be seen, a portion of the high-purity olefin from the countercurrent blowdown step was compressed to the feed pressure and used for rising the bed cocurrently in step 3. Purging with the strongly adsorbed component results in a significant increase in the purity of that component in the product stream. Here, the product of the high-pressure rinse step is recycled and mixed volumetrically, with the feed gas supplied to step 2.

The objective of this example was to compare the performance of the adsorbents employing equilibrium separations, kinetic separation, and separation by exclusion of one of the components. The comparison needed to be carried out using nearly identical cycle conditions. In the case of ethane/ethylene separation, the adsorbents were compared at the same product throughput and the product purity was studied at various product recoveries. In the case of propane/propylene separation, the adsorbents had highly differing productivities, and hence the comparison was done at constant product purity and the product throughput was studied at various values of product recovery. It should be noted that the term "product" mentioned throughout this work refers to the olefin-rich product obtained in desorption step 4 unless otherwise specified. The various process variables in this work were defined as follows:

Product recovery is as defined in equation 1.

Purge-to-feed ratio (P/F) is as defined in equation 2.

Another important parameter used to gauge the adsorbent's productivity is the product throughput (also referred to as productivity in this work):

Production throughput is as per equation 3.

PSA Simulation

The model used assumes the flow of a gaseous mixture of two components in an adiabatic fixed bed packed with spherical adsorbent particles of

identical size and shape. Axial dispersion for mass and heat transfer is assumed, but dispersion in the radial direction is taken to be negligible. Axial pressure drop is neglected and ideal gas law is assumed to hold since pressures involved are low. External mass-transfer limitations are assumed to be negligible. Also the gas is
 5 assumed to have constant viscosity and heat capacity.

The mass-balance equation for component k in the bed is given by the axially dispersed plug flow equation (Sun et al., 1996): See equation 4.

The overall material balance obtained is as per equation 5.

For adiabatic bed with no heat transfer with the surroundings, the
 10 overall heat balance may be written as per equation 6.

The axial dispersion coefficient (D_{ax}) and effective thermal conductivity (λ_1) were obtained from the mass and thermal Peclet numbers, respectively, which were obtained using standard correlations for dispersion in fixed beds (Yang, 1987).

15 The rate of uptake by a sorbent particle was assumed to follow the linear driving force (LDF) approximation, which holds true when $D_e t / R_p^2 > 0.1$ as per equation 7, where q_k^* is the equilibrium amount adsorbed at the surface of the pellet. The LDF approximation was valid under the conditions used in this study.

Cross-term diffusivities were neglected. The effective diffusivity
 20 values ($D_{e,k}$) were assumed to be independent of the surface coverage, and they were assumed to have an exponential temperature dependence per equation 8, where $D_{e,k}^0$ was the effective diffusivity at a reference temperature T_{ref} .

The initial conditions of each step were the conditions at the end of the preceding step. For the first step, the bed was maintained at 0.1 atm with a certain
 25 composition of the olefin/paraffin mixture. The pressurization and the countercurrent blowdown steps were the only pressure-changing steps and the variation of pressure with time was assumed to be exponential as per equation 9, where t_s was conveniently chosen time constant. The value of t_2 has to be chosen sufficiently small so as to obtain the desired pressure change but also sufficiently large so as to

keep the (dP/dt) term in the model small enough to avoid stiffness in the numerical method used. In general, t_s was 24-27% of the step time chosen.

The boundary conditions used were the Dankwerts' boundary conditions for the closed/closed vessel case as per equation 10.

5 Here $z = 0$ and $z = L$ represent the entrance and exit points in the fixed bed, respectively. The subscript m refers to the number of the step in the cycle.

For adsorption by π -complexation, the equation giving the most satisfactory fit to experimental data has been known to be the Langmuir-uniform-distribution (LUD) equation (Yang and Kikkinides, 1995; Chen and Yang, 1995).

10 Both the physisorption and chemisorption terms were included in the isotherm. At present, however, no equation is available for its extension to multicomponent mixtures. Hence, the loading ratio correlation (LRC) extended to binary mixtures was used (Yang, 1987) as per equation 11,

where q_m , b and n were LRC parameters. The temperature dependence of q_m and b was given as per equation 12.

15 The coupled partial differential equations were solved using an implicit finite difference scheme employing the Crank-Nicolson method (Carnahan et al., 1969). The fixed bed was discretized into 100 spatial points and time into 200 time steps. The details of the numerical scheme used are given elsewhere (Sun et al., 20 1996). The PSA code was written in FORTRAN and was executed using a SUN-SPARC workstation. The model and numerical method were found to be stable and convergent for all of the runs, and all mass balances were found to be valid within 4% relative error. The machine time required for computation of one PSA cycle was about 15-20 s, and the cyclic steady state was reached in 200-500 cycles, depending 25 upon the initial conditions used.

Results and Discussion

Isotherms and Diffusivities on 4A Zeolite

The pure-component equilibrium isotherms of C_2H_4 and C_2H_6 on 4A zeolite at 25°C and 70°C are shown in Figure 29. The equilibrium data were fitted

well by the LRC model shown in Eq. 11. The fitting parameters were shown in Table 1. From Figure 29, the amounts adsorbed at 25 °C and 1 atm for C₂H₄ and C₂H₆ were 2.8 and 2.4 mmol/g, respectively. Hence, equilibrium separation would not be feasible.

5 Uptake rates were measured using Micromeritics ASAP 2010 at 25 °C and 70 °C, and the results are shown in Figure 30. The pressure increments were from 0 atm to 0.1 atm. At 25 °C, after 15 s, C₂H₄ adsorption was approximately 75% complete, while C₂H₆ adsorption was only 15% complete. Diffusion time constants, D/R^2 , were calculated by fitting experimental data with the solution for the diffusion
10 equation for spherical particles (Kärger and Ruthven, 1992). The values of D/R^2 obtained for C₂H₄ and C₂H₆ at 25 °C were 5.12×10^{-3} and 1.64×10^{-4} , L/s⁻¹, respectively. The ratio of these diffusivities was 31, which was similar to the ratio of pure-component diffusivities of O₂/N₂ in the commercial separation of air using a carbon molecular sieve. However, it was observed that the desorption rate of the
15 C₂H₄ on zeolite 4A was low compared to that of adsorption rate, thus giving it an irreversible nature. Unlike C₂H₄, C₂H₆ adsorption was completely reversible at this temperature.

For purpose of simulation, however, the adsorption and desorption rates were assumed to be equal. The results of the simulation would thus represent
20 the best separation of C₂H₄ and C₂H₆ by zeolite 4A at 25 °C.

Equilibrium isotherms and diffusion time constants of C₃H₆ and C₃H₈ on 4A zeolite were also measured. The isotherms are shown in Figure 31, and the uptake rates of C₃H₆ are shown in Figure 32. It is noteworthy that C₃H₈ was essentially excluded from the 4A zeolite, whereas the C₃H₆ molecule was free to
25 diffuse. The effective aperture size of the 4A zeolite is 3.8 Å, which obviously is the demarcation between the kinetic diameters of C₃H₆ and C₃H₈. The diffusion time constants of C₃H₆ at 25 °C and 120 °C were 8.5×10^{-5} L/s⁻¹ and 4.3×10^{-4} L/s⁻¹, respectively. The temperature-dependent diffusivity values are included in Table 2. The equilibrium LRC fitting parameters are given in Table 1.

It was observed that the adsorption of C_3H_6 in the 4A zeolite was not completely reversible at 25°C, with approximately 10% adsorbate remaining after desorption. However, the adsorption at 120°C was readily reversible.

Isotherms and Diffusivities on the Carbon Molecular Sieve

5 Unlike the 4A zeolite with a discrete aperture dimension, the CMS had a distribution of micropore sizes ranging from 3 Å to 5 Å. Measurements with C_3H_6 and C_3H_8 showed that these molecules were totally excluded. The equilibrium isotherms of C_2H_4 and C_2H_6 at various temperatures are shown in Figure 33. C_2H_6 was nearly excluded, yet detectable amounts were observed due to the larger pores in
10 the CMS.

The diffusion time constants for C_2H_4 in CMS were 1.90×10^{-6} L/s⁻¹ at 25°C and 1.77×10^{-5} L/s⁻¹ at 100°C. The isotherm parameters are given in Table 1, and the temperature-dependent D/R^2 values are included in Table 2. Although the diffusivities were low, the equilibrium selectivity for C_2H_4/C_2H_6 was high. Hence, the
15 C_2 /CMS system was included in PSA simulation.

Equilibrium Isotherms and Diffusivities on Monolayer $AgNO_3/SiO_2$

Both C_2H_4/C_2H_6 and C_3H_6/C_3H_8 separations are effective with the $AgNO_3/SiO_2$ π -complexation sorbent, as shown in prior examples 1 to 3. Here, only C_3H_6/C_3H_8 was included for comparison with the other adsorbents. The Ag-resin was
20 used for the C_2 separation for the purpose of evaluating separation by π -complexation. Data for C_2H_4 and C_2H_6 isotherms and diffusivity values were taken from the work by Wu et al. (1997) and are presented in Tables 1 and 2, respectively.

The equilibrium isotherms of C_3H_6 and C_3H_8 and on $AgNO_3/SiO_2$ at 25°C and 70°C are shown in Figure 34. The Langmuir-type isotherm (i.e., LRC) did
25 not fit the data well due to the steepness of the equilibrium data. The best fit is shown in Figure 34, and the fitting parameters are included in Table 1. Since the fitted isotherm undercalculated the Δq in the PSA cycle, the PSA simulation result based on the fitted isotherm would underestimate the separation.

The uptake rates were rapid and not shown here for example, the diffusion time constants for C_3H_6 and C_3H_8 at $70^\circ C$ were $1.67 \times 10^{-3} L/s^{-1}$ and $1.48 \times 10^{-2} L/s^{-1}$, respectively. The temperature-dependent values are included in Table 2. The rapid diffusion was due to the large pore dimensions ($32\text{\AA}$) in the sorbent.

5 Ethane/Ethylene Separation Using Comparative Adsorbents

The adsorbents that were considered for ethane/ethylene separation were zeolite 4A, Bergbau-Forschung carbon molecular sieve (CMS), and Ag^+ -exchanged Amberlyst-35 resin. As discussed earlier, zeolite 4A had a good capacity for ethylene separation by way of kinetic separation, whereas the Bergbau-Forschung
10 CMS had the property of excluding ethane completely. Recently, Ag^+ -exchanged Amberlyst-35 with 36.5% degree of ion exchange (DIE) was found to have promising prospects for olefin/paraffin separation applications by virtue of steep isotherms for ethylene and comparatively flat isotherms for ethane (Wu et al., 1997).

The PSA cycle used is outlined in Table 3. In the case of zeolite 4A, a
15 feed temperature of $25^\circ C$ was used with time for each step ranging from 80 to 480 s. As was mentioned earlier, the desorption rate of C_2H_4 on zeolite 4A was low compared to that of absorption at $25^\circ C$. In the present work, however, this irreversibility is neglected and equal rates of absorption and desorption are assumed, thus giving the best separation possible by this sorbent. The purge-to-feed ratio was
20 adjusted for each cycle time so as to provide an optimum product purity and recovery.

For Ag^+ -exchanged resin, a feed temperature of $25^\circ C$ was also employed for comparison with 4A zeolite. A study of the uptake curves for C_2H_4 provided by Wu et al. (1997) shows a 90% uptake after 30 min duration. Hence step
25 times ranging from 800 s to 1,800 s were used.

The performance of the sorbents needed to be compared by keeping one of the following three parameters constant product purity, product recovery, and product throughput. As comparable product throughputs were obtained in the case of zeolite 4A and the Ag^+ -Amberlyst-35, comparison was done by studying the product

purity vs. product recovery at an average product throughput of about 1.1×10^{-4} kg product/h/kg adsorbent. The PSA cycle conditions used in the simulation runs are given in Table 4 and the results of the simulations are shown in Figure 35. The dots in the figure represent actual results of the simulation runs, while the line indicates the trend followed. As can be seen from the figure, the C_2H_4 product purity fell rapidly at high C_2H_4 product recovery for both the sorbents at constant productivity. High recovery was possible at low product purities, but it fell drastically at very high purity in the case of zeolite 4A. However, in the case of Ag^+ -Amberlyst-35 resin sorbent, much higher C_2H_4 product recovery was possible compared to zeolite 4A at corresponding product purity and at the constant product throughput under consideration. Although, in general, the runs for Ag^+ -resin show a slightly lower product throughput than that for zeolite 4A, comparison between runs 1 and 2 for Ag^+ -resin and runs 6 and 7 for zeolite 4A in Table 4 is valid, since product throughputs are about the same for both. Hence, it can be concluded that equilibrium separation by π -complexation adsorbents such as Ag^+ -Amberlyst-35 gives better performance than kinetic separation using zeolite 4A. Moreover, both curves in Figure 35 could be raised by further lowering the product throughput. Although product purities in excess of 99.9% were possible for the Ag^+ -resin at recoveries lower than 10%, the product throughput dropped further. Hence these data could not be shown in this figure. The monolayer $AgNO_3/SiO_2$ sorbent of the invention has selectivity for ethylene similar to that of Ag^+ -resin and in addition has much higher diffusivities compared to the latter sorbent. Hence the disadvantage of having low product throughputs for Ag^+ -resin can be overcome by using the $AgNO_3/SiO_2$ sorbent with negligible diffusion limitation.

Simulation studies were also carried out for Bergbau-Forschung CMS. It can be seen from the C_2H_4/C_2H_6 isotherms in Figure 33 that C_2H_6 was excluded almost completely from the pores, whereas C_2H_4 is not. A study of the C_2H_4 uptake curves for CMS showed that the uptake was very slow, requiring more than 1 h to reach 80-90% of uptake for C_2H_4 , even at a high temperature of $100^\circ C$. Simulation runs were carried out at $100^\circ C$ with a step time ranging from 4,000 to 8,000 s. Since

the cycle time was high, the product throughput was very low compared to that of zeolite 4A and Ag⁺-Amberlyst-35. Also, since the working capacity of the CMS adsorbent for C₂H₄ was quite small compared to that possessed by the other two adsorbents, there was a large restriction on the feed throughput and on the allowable
5 purge-to-feed ratio. The results of PSA simulations showed that although product purities over 90% were possible, the product recoveries would not exceed 5%. The low diffusivity of the olefin caused the feed to break through the bed even at interstitial velocities as low as 0.05 m/s, thus causing considerable loss of olefin in the feed product. Even at lower product purities, the recoveries did not improve
10 much. Further, the maximum product throughput that could be achieved was of the order of 1.4×10^{-5} kg/h/kg sorbent, which is only 1% of that possible by zeolite 4A and Ag⁺-resin. It was thus obvious that the performance of Bergbau-Forschung CMS as a sorbent for C₂H₄/C₂H₆ was very poor compared to the other sorbents despite having the property of excluding C₂H₆.

15 Several observations are evident to this point based on ethane/ethylene separation of Examples 1 to 4. The monolayer (thermally dispersed) AgNO₃/SiO₂ sorbent of the invention performed better than the carbon molecular sieve, the Ag⁺ resin and the zeolite 4A. The prior examples 1-3 showed that impregnated AgNO₃/SiO₂ (incipient wetness) performed even better.

20 Propane/Propylene Separation

For the case of propane/propylene, the adsorbents that were considered for separation were zeolite 4A and monolayer AgNO₃/SiO₂. Zeolite 4A almost excludes propane from its pores, as can be seen from Figure 31, and hence makes it an excellent prospect for C₃H₆/C₃H₈ separation. The AgNO₃/SiO₂ adsorbent
25 of the invention possesses a good selectivity, steep isotherm, and hence a large working capacity for C₃/H₆ compared to that for C₃H₈. Thus this sorbent, which employs equilibrium separation due to π -complexation, is also a good candidate for this separation. The Bergbau-Forschung CMS adsorbent was found to exclude both

C_3H_6 and C_3H_8 from its pores, and hence it was not considered for this olefin/paraffin system.

The PSA cycle used for C_3H_6/C_3H_8 separation was identical to that used for C_2H_4/C_2H_6 separation discussed earlier. In the case of zeolite 4A, separation was due to the difference in diffusion rate of the two species, and hence the cycle time had to be optimized. From a study of the uptake curves shown in Figure 32, it was decided to use step times ranging from 100 s to 800 s. As opposed to this, the $AgNO_3/SiO_2$ sorbent was found to have very fast uptake rates, and hence short step times of 60 to 400 s were used. The feed temperatures in the case of zeolite 4A and $AgNO_3/SiO_2$ were 100°C and 70°C, respectively.

The results of the PSA simulations are shown in Figure 36. The corresponding cycle conditions for the runs shown in the figure are summarized in Table 5. Since the product throughputs obtained for the two sorbents were quite different, the product recovery and purity could not be compared at the same product throughput, as was done in case of C_2H_4/C_2H_6 separation. Instead, the C_3H_6 product throughput of the two sorbents was compared at the same product purity of about 99%. As can be seen from Figure 36, $AgNO_3/SiO_2$ sorbents gave almost five times the product throughput as was given by zeolite 4A. It should be noted that the main purpose of this example was to compare the performance of two types of sorbent under nearly identical cycle conditions rather than provide the optimal performance of each sorbent. The product recovery can be increased by further decreasing the product throughput or decreasing the product purity. For both sorbents, product recoveries in excess of 70% were possible when product purity was lowered to 95% at product throughput of the order of 1×10^{-3} kg of product/h/kg of adsorbent.

It was interesting to note the parabolic nature of product throughput vs. product recovery curve at constant product purity for $AgNO_3/SiO_2$. There appeared to be an optimal productivity at a particular recovery. For a PSA cycle, the aforementioned three performance variables are interrelated in a complex manner. The data points for $AgNO_3/SiO_2$ in Figure 36 at lower recovery values were obtained at short step times, whereas those at higher recovery values were those at long step

times, as can be seen in Table 4. The capacity of the sorbent was utilized to a greater extent when step time was increased. Moreover, less of the olefin was wasted as a product of the feed step, and hence recovery was seen to improve with an increase in step time. Hence, as the step time was increased from a low value, there was initially
5 a rise in productivity as well as product recovery. However, with further increase in step time, the number of cycles performed per hour decreased, thus resulting in decrease in product throughput. In addition, as the time was increased, the less-adsorbed component, that is, C_3H_8 , also diffused to a greater extent. This is more so for separation by $AgNO_3/SiO_2$ than by zeolite 4A because C_3H_8 has greater
10 diffusivity with a higher temperature dependence than that of C_3H_6 for the former sorbent, as can be seen from Table 2. Hence, as per definition (Eq. 3), the product throughput decreased with higher step times, thus giving parabolic curve.

Multiplicity of Cyclic Steady States for $AgNO_3/SiO_2$

The transient C_3H_6 product purity vs. the cycle number was studied at
15 adsorption pressure of 1 atm, desorption pressure of 0.1 atm, feed temperature of $70^\circ C$, step time of 210 s, time constant (t_s) of 50 s, and purge velocity of 0.186 m/s. The bed was initially saturated at 0.1 atm with a mixture of 5% C_3H_6 at $70^\circ C$. The variation of product purity as the system approached cyclic steady state at different feed velocities is shown in Figure 37. A sudden jump of product purity from 80% to
20 98% was observed as purge velocity was increased from 0.80 m/s to 0.81 m/s. The transient product purity curves at intermediate feed velocity values showed a sigmoidal nature. It seemed as if the system tended toward an intermediate steady state (seemingly an unstable state), but then bifurcated to approach two different steady states. The product purity obtained at different feed velocities at the same
25 purge velocity of 0.186 m/s is shown in Figure 38. All the other conditions were fixed at the values given earlier. For an initial temperature of $70^\circ C$, the product purity remained at 79.9% as feed velocity was increased from 0.72 m/s to 0.80 m/s (lower branch of Figure 31). Thereafter, at feed velocity of 0.80 m/s and beyond, the product purity suddenly increased to 98.4%. At the same time, product recovery

suddenly decreased from 41% to 28% as feed velocity was increased from 0.80 m/s to 0.81 m/s. In another set of simulations, keeping all the other parameters the same, the product purity was studied at different feed velocities with an initial temperature of 120°C. In this case, the product purity and product recovery remained at 79.9% and 41%, respectively, until feed velocity of 0.75 m/s. Beyond this value, the product purity jumped to 98.8% and the product recovery decreased to 28% (upper branch of Figure 38). Thus, for the range of feed velocities from 0.75 m/s to 0.80 m/s, two different cyclic steady states were observed with respect to initial temperature of the PSA bed. Kikkinides et al. (1995) had seen a similar behavior of multiplicity for the system of $\text{H}_2\text{S}/\text{CO}_2/\text{CH}_4$ on 5A zeolite. In their case, multiplicity of steady states was observed with respect to different initial concentrations of the sorbates. However, in the present work, simulations carried out with different initial concentrations did not display multiplicity of periodic steady states.

A similar type of behavior was observed with change in purge velocity. As before, when the initial temperatures of the bed were altered from 70°C to 120°C, the system displayed multiple steady states for a range of purge velocities. Figure 39 displays the transient product purity profiles as the system approaches cycle steady state for adsorption pressure of 1 atm, desorption pressure of 0.1 atm, feed temperature of 70°C, step of 210 s, time constant (t_s) of 50 s, feed velocity of 0.80 m/s, and purge velocity ranging from 0.18 m/s to 0.19 m/s. The approach to a middle unstable state and then its bifurcation to upper and lower stable steady states seen in Figure 39 was similar to that in Figure 37. The effect of the interstitial purge velocity on the C_3H_6 product concentration starting from two different initial temperatures is shown in Figure 40. The lower branch in the figure represents the product purities obtained when the bed was started with an initial temperature of 70°C. As the purge velocity was increased from 0.186 m/s to 0.187 m/s, the product purity suddenly increased to 98.4% from 80%. The upper branch was obtained by starting with an initial temperature of 120°C, and a similar jump was seen at 0.184 m/s. Thus, for the small range of purge velocities between 0.184 m/s and 0.186 m/s, multiple steady states were observed with respect to the initial temperature of the

bed. A further study of the effect of initial temperature on the product-purity dependence of feed and purge velocity in the region of multiplicity revealed that all simulations carried out at initial temperatures below 106°C followed the behavior observed for the initial temperature of 70°C, whereas all initial temperatures above
5 107°C gave the behavior observed for the that of 120°C.

The performance of three types of adsorbents, namely, those involving kinetic separation, exclusion of one of the components, and equilibrium separation, was compared for C₂H₄/C₂H₆ and C₃H₆/C₃H₈ systems using PSA simulations of a four-step cycle involving cocurrent purge with the strongly adsorbed species, that is,
10 olefin. In case of the ethane/ethylene system, the performance of AgNO₃/SiO₂ as per prior Examples 1-3 was very attractive. Equilibrium separation using Ag⁺-exchanged Amberlyst-35 sorbent was found to be superior compared to the kinetic separation carried out by zeolite 4A by a study of the product purity vs. recovery curve at constant product throughput. The performance of carbon molecular sieve, which was
15 found to exclude C₂/H₆ from the pores, was found to be poor compared to both zeolite 4A and Ag⁺-exchanged resin, mainly because of its slow uptake rates. The performance of AgNO₃/SiO₂ prepared by incipient wetness method was the most attractive for ethane/ethylene separation.

For the propane/propylene separation, equilibrium separation by
20 monolayer AgNO₃/SiO₂ sorbent was found to be superior to the kinetic separation by zeolite 4A. In this case comparison was performed by comparing the product throughputs obtained using the two sorbents at a fixed C₃H₆ product purity of 99.1%. For C₃H₆/C₃H₈ separation on AgNO₃/SiO₂ sorbent, multiplicity of cyclic steady states was observed within certain ranges of feed and purge velocities. Within these
25 ranges, simulation of the PSA starting from two different initial conditions while keeping the same operating conditions yielded two different stable cyclic steady states.

Spreading of monolayer AgNO₃ on various substrates by the incipient wetness technique is thought to be the preferred method for preparing adsorbents.

The preferred $\text{AgNO}_3/\text{SiO}_2$ prepared by incipient wetness avoids decomposition of the metal compound which seems to occur with thermal dispersion heating.

Table A. Fitting parameters for isotherms of C_2H_4 (eq. 2) and C_2H_6 (eq. 1) at 70°C on SiO_2 and $\text{AgNO}_3/\text{SiO}_2$ prepared by thermal monolayer dispersion and incipient wetness impregnation.

C_2H_4		q_{mp}	q_{bp}	q_{mc}	b_c
	SiO_2	1.12	0.47	--	--
	Monolayer $\text{AgNO}_3/\text{SiO}_2$	0.18	1.78	1.61	0.20
	Wet impregnated $\text{AgNO}_3/\text{SiO}_2$	0.30	3.76	4.16	0.02
C_2H_6					
	SiO_2	0.96	0.34	--	--
	Monolayer $\text{AgNO}_3/\text{SiO}_2$	0.18	1.78	--	--
	Wet impregnated $\text{AgNO}_3/\text{SiO}_2$	0.27	6.6	--	--

Table B. BET surface areas (m^2/g) for monolayer AgX/SiO_2 ($\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{I}$)

	AgF/SiO_2	546
10	AgCl/SiO_2	486
	AgBr/SiO_2	479
	AgI/SiO_2	405

Table C. Fitting parameters for equilibrium isotherms of C_3H_6 on monolayer AgX/SiO_2 (where $X = F, Cl, Br, I$) at $70^\circ C$ using eq. (2).

	q_{mp} (mmol/g)	q_{bp} mmol/g	q_{mc} mmol/g	b_c atm^{-1}	s	
5	AgF/SiO ₂	2.33	0.4	3.23	0.03	7
	AgCl/SiO ₂	2	0.3	3.22	0.04	7
	AgBr/SiO ₂	1.99	0.43	3.5	0.03	7
	AgI/SiO ₂	3.1	0.19	3.8	0.03	7

Table D. Fitting parameters for C_3H_6 adsorption at $70^\circ C$ on $AgNO_3/Al_2O_3$, SiO_2 , MCM-41.

		q_{mp}	q_{bp}	q_{mc}	b_c
		mmol/g	mmol/g	mmol/g	atm ⁻¹
10	AgNO ₃ /Al ₂ O ₃	2.12	0.03	1.9	0.04
	AgNO ₃ /SiO ₂	1.49	0.43	3.16	0.76
	AgNO ₃ /MCM-41	1.19	0.62	6.63	0.01

Table E. Diffusion time constants (D/R^2) for C_3H_6 on $AgNO_3/Al_2O_3$, $AgNO_3/SiO_2$ and $AgNO_3/MCM-41$ prepared by incipient wetness technique.

		D/R^2 (s^{-1})		BET Surface Area	Pore Size
		25°C	70°C	m^2/g	Å
5	$AgNO_3/Al_2O_3$	4.9×10^{-3}	5.8×10^{-3}	228	18
	$AgNO_3/SiO_2$	2.3×10^{-3}	3.5×10^{-3}	398	8
	$AgNO_3/MCM-41$	8.5×10^{-3}	1.4×10^{-2}	621	29

Table 1. Parameters in the Temperature-Dependent Loading Ratio Correlation Isotherms of C₂H₄, C₂H₆, C₃H₆ and C₃H₈ for Adsorbents

Sorbent	Sorbate	k ₁ (mmol/g)	k ₂ (K)	k ₃ (atm ⁻ⁿ)	k ₄ (K)	n	-ΔH (ca /K)	
5	Zeolite 4A	C ₂ H ₄	2.462	3.529 x 10 ⁻¹	1.38 x 10 ⁻⁶	5,927	1.41	11.9
	Zeolite 4A	C ₂ H ₆	5.956 x 10 ⁻¹	4.232 x 10 ²	9.00 x 10 ⁻⁵	3,599	1.24	7.15
	Zeolite 4A	C ₃ H ₆	7.232 x 10 ⁻¹	3.449 x 10 ²	2.81 x 10 ⁻⁵	4,712	0.82	9.36
	Zeolite 4A	C ₃ H ₈	2.71	----	4.6 x 10 ⁻³	----	0.46	----
	Ag ⁺ -resin	C ₂ H ₄	2.94 x 10 ⁻²	1.290 x 10 ³	2.49 x 10 ⁻¹	632	0.67	9.35
10	Ag ⁺ -resin	C ₂ H ₆	4.53 x 10 ⁻⁴	1.829 x 10 ³	2.00 x 10 ⁻³	0.0	2.17	4.6
	CMS	C ₂ H ₄	0.393	3.911 x 10 ²	5.38 x 10 ⁻¹	568	0.98	3.25
	CMS	C ₂ H ₆	1.0 x 10 ⁻⁶	3734	9 x 10 ⁻²	200	0.5	----
	AgNO ₃ /SiO ₂	C ₃ H ₆	1.09 x 10 ⁻¹	1.169 x 10 ³	9.41 x 10 ⁻²	811	0.68	11.5
	AgNO ₃ /SiO ₂	C ₃ H ₈	4.09 x 10 ⁻¹	1.743 x 10 ³	2.02 x 10 ⁻³	270	0.69	3.35

Table 2. Parameters Used in Calculating Temperature-Dependent Overall Diffusion Time Constant (D_ℓ/R^2) for Diffusion of C_2H_4 , C_2H_6 , C_3H_6 and C_3H_8 in Adsorbents Used (Eq. 8)*

Sorbent	Sorbate	D^o/R^2 (s ⁻¹)	E_{act}/R_g (K)	
5	Zeolite 4A	C ₂ H ₄	5.12 x 10 ⁻³	1,477
	Zeolite 4A	C ₂ H ₆	1.64 x 10 ⁻⁴	1,231
	Zeolite 4A	C ₃ H ₆	8.49 x 10 ⁻⁵	2,051
	Zeolite 4A	C ₃ H ₈	----	----
	Ag ⁺ -resin	C ₂ H ₄	1.03 x 10 ⁻⁴	766
10	Ag ⁺ -resin	C ₂ H ₆	1.07 x 10 ⁻⁴	558
	CMS	C ₂ H ₄	1.89 x 10 ⁻⁶	3,438
	CMS	C ₂ H ₆	----	----
	AgNO ₃ /SiO ₂	C ₃ H ₆	1.43 x 10 ⁻³	352
	AgNO ₃ /SiO ₂	C ₃ H ₈	8.7 x 10 ⁻³	1,206

* T_{ref} = 298 K.

Table 3. Adsorption Bed Characteristics and Operating Conditions Used in the PSA Simulations

5	Bed Length	3.0 m
	Diameter of adsorber bed	1.0 m
	Bed external porosity	0.40 m
	Bed density	720 kg/m ₃
	Heat capacity of bed	0.28 cal/g/k
10	Wall temperature	298 K (ambient)
	Feed gas composition	50% olefin, 50% paraffin
	Adsorption pressure (P_H)	1.0 bar
	Desorption pressure (P_L)	0.1 bar
	Initial total pressure	0.1 bar
	Axial dispersion coefficient (D_{ax})	3.8 x 10 ⁻² m ² /s
	Effective thermal conductivity (λ_L)	2.2 x 10 ³ W/m/K

Table 4. PSA Operating Parameters for Comparison of Performances of Zeolite 4A and Ag⁺-Exchanged Amberlyst-35 Resin for the Separation of C₂H₄ and C₂H₆*

Run No.	Time		Interstit.		Interstit.		Desorp.		Desorp.		Desorp. Product	
	Step		Const.		Feed		Purge		Product		Product	
	Time	(s)	t ₃	(s)	Vel. U _H	(m/s)	Vel. U _p	(m/s)	(C ₃ H ₆)	% Purity	C ₃ H ₆	% Recovery
<i>Ag⁺ - Resin (Feed temperature = Initial temperature = 25 °C)</i>												
5	1,800	450	0.40	0.01	0.01	0.135	8.81	99.73	0.062	0.058	0.061	0.054
	800	200	0.15	0.02	0.02	0.062	22.46	91.92	0.062	0.058	0.061	0.054
	1,200	300	0.10	0.05	0.05	0.058	41.12	83.86	0.058	0.058	0.061	0.054
	1,000	250	0.10	0.01	0.01	0.061	41.38	81.26	0.061	0.061	0.061	0.054
	1,380	345	0.08	0.01	0.01	0.054	48.73	85.09	0.054	0.054	0.054	0.054
<i>Zeolite 4A Sorbent (Feed temperature = Initial temperature = 25 °C)</i>												
10	80	15	1.30	0.15	0.15	0.109	1.32	96.33	0.109	0.109	0.109	0.109
	480	120	0.10	0.03	0.03	0.032	7.18	79.83	0.032	0.032	0.032	0.032
	80	15	0.30	0.10	0.10	0.292	26.71	73.91	0.292	0.292	0.292	0.292
	120	30	0.10	0.08	0.08	0.160	34.50	73.19	0.160	0.160	0.160	0.160

10	300	80	0.05	0.03	65.29	45.33	0.116
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$*P_H$ 1.0 atm; $P_L = 0.1$ atm

Table 5. PSA Operating Parameters for Comparison of Performances of Zeolite 4A and Monolayer $\text{AgNO}_3/\text{SiO}_2$ for the Separation of C_3H_6 and C_3H_8^*

Run No.	Step Time (s)	Time		Interstit.		Interstit.		Desorp.		Desorp. Product (C ₃ H ₆) Throughput (kg of Product/h/10 ³ of Adsorbent) 10 ³
		Const.	t ₃	Interstit.		Interstit.		Desorp.		
				Feed	Purge	Product	Product	C ₃ H ₆	C ₃ H ₆	
5 AgNO ₃ /SiO ₂ Sorbent (Feed temperature = Initial temperature = 70 °C)										
1	60	16	1.40	0.90	98.57	18.08	1.79			
2	60	16	1.40	0.80	97.60	24.12	2.19			
3	150	35	1.00	0.32	99.03	27.97	1.87			
4	400	110	0.20	0.10	99.05	43.58	0.65			
10 Zeolite 4A sorbent (Feed temperature = Initial temperature = 100 °C)										
5	100	30	0.80	0.13	99.94	7.95	0.31			
6	400	110	0.70	0.05	99.10	10.54	0.36			
7	400	110	0.60	0.05	99.01	12.16	0.40			

8	800	240	0.80	0.045	99.97	23.59	0.10
9	600	150	0.10	0.065	99.98	27.29	0.15

* $P_H = 1.0$ atm; $P_L = 0.1$ atm

Notation Used in Examples 1-3

	b	Langmuir constant, atm ⁻¹
	D	diffusivity, cm ² /s
	P	pressure, atm
5	q	equilibrium amount absorbed, mmol/g
	q _m	monolayer or saturated amount absorbed, mmol/g
	r	particle radius, cm
	s	heterogeneity parameter
	X	halides (F, Cl, Br, I)
10	Subscripts	
	c	chemisorption or π -complexation
	p	physical adsorption

Notation Used in Example 4

	C _p	= specific heat, kcal/g/K
15	E _{act}	= diffusional energy of activation, kcal/mmol
	ΔH	= heat of adsorption, kcal/mol
	L	= total length of the adsorption bed, m
	P	= total pressure
20	$\bar{q}$	= volume pressure bar
	R	= gas constant, kcal/mmol/K
	R _p	= radius of particle, m
	t	= time, s
	T	= temperature, K

- u = interstitial gas velocity, m/s
 y = mole fraction of the components in the gas phase
 z = axial coordinate in the bed, m
 ϵ = void fraction of the packing
5 ϵ_t = bed void fraction including macropores in particles

Product recovery =

$$\frac{(\text{C}_3\text{H}_6 \text{ from step 4}) - (\text{C}_3\text{H}_6 \text{ used for purging in step 3})}{(\text{C}_3\text{H}_6 \text{ fed in step 1 and step 2})} \quad (1)$$

$$\text{Purge-to-feed ratio (P/F)} = \frac{(\text{C}_3\text{H}_6 \text{ used to purge in step 3})}{(\text{C}_3\text{H}_6 \text{ fed in step 1 and step 2})} \quad (2)$$

Product throughput

$$= \frac{\text{Amount (kg) of C}_3\text{H}_6 \text{ produced per hour}}{\text{Amount (kg) of adsorbent}} \quad (3)$$

$$\epsilon_t \frac{\partial y_k}{\partial t} - \epsilon D_{ax} \frac{\partial^2 y_k}{\partial z^2} + \epsilon \frac{\partial (uy_k)}{\partial z} + \frac{\rho_b RT}{P} \frac{\partial \bar{q}_k}{\partial t} + \frac{\epsilon_t y_k}{P} \frac{dP}{dt} = 0. \quad (4)$$

The overall material balance obtained is

$$\epsilon \frac{\partial u}{\partial z} = - \frac{\rho_b RT}{P} \sum_{k=1}^2 \frac{\partial \bar{q}_k}{\partial t} - \frac{\epsilon_t}{P} \frac{dP}{dt} \quad (5)$$

$$\left[\epsilon \rho_g c_{pg} + \rho_b \left(c_{ps} + \sum_{k=1}^2 \bar{q}_k c_{pg} \right) \right] \frac{\partial T}{\partial t} + \epsilon \rho_g c_{pg} u \frac{\partial T}{\partial z} - \epsilon \lambda_L \frac{\partial^2 T}{\partial z^2} = \rho_b \sum_{k=1}^2 |\Delta H_j| \frac{\partial \bar{q}_k}{\partial t} + \epsilon \frac{dT}{dt} \quad (6)$$

$$\frac{\partial \bar{q}_k}{\partial t} = \frac{15 D_{e,k}}{R_p^2} (q_k^* - \bar{q}_k), \quad (7)$$

$$D_{e,k} = D_{e,k}^0 \exp \left[\frac{-E_{act,k}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right], \quad (8)$$

$$P(t) = P_{fin} + (P_{ini} - P_{fin}) \exp(-t/t_s), \quad (9)$$

$$\begin{aligned} D_{ax} \frac{\partial y_k}{\partial z} \Big|_{z=0} &= u_m(y_k|_{z=0} - y_{H,k}) \\ -\lambda_L \frac{\partial T}{\partial z} \Big|_{z=0} &= \rho_g c_{pg} u_m(T|_{z=0} - T_H) \\ \frac{\partial y_k}{\partial z} \Big|_{z=L} &= \frac{\partial T}{\partial z} \Big|_{z=L} = 0. \end{aligned} \quad (10)$$

$$q_k^* = \frac{q_{m,k} b_k P^{n_k}}{1 + \sum_{j=1} b_j P^{n_j}}, \quad (11)$$

$$q = \frac{q_{mp} b_b P}{1 + b_p P} \quad (A)$$

$$q = \frac{q_{mp} b_b P}{1 + b_p P} + \frac{q_{mc}}{2s} \ln \frac{1 + b_c P e^s}{1 + b_c P e^{-s}} \quad (B)$$

The present invention further provides improved methods and sulfur resistant adsorbents for separating a diene from a mixture which includes such diene. The invention is particularly useful for separating dienes having four to eight carbons from corresponding mono-olefins having four to eight carbons. Improved separation methods are needed due to the close boiling points of the C₄ to C₈ dienes and their corresponding C₄ to C₈ mono-olefins. Selected examples are as follows with numerical values being the boiling points in degrees centigrade 1,2- and 1,3-butadiene respectively 10.8 and -4.4; 1-butene, 2-butene cis and trans, respectively -6.3, 3.7 and 0.9; 1,3-, 1,4-, 1,5- and 2,4-hexadiene respectively 73, 65, 59.5, and 80; 1-hexene, 2-hexene cis and trans and 3-hexene cis and trans respectively 63.3, 68.8, 68, 66.4, and 67.1; and 1,7- and 2,6- octadiene at 113-8 and 118-20; and 1-, 2-, 3-, and 4-octene in a range of 121.3-125.6; all according to the 62nd Edition of the CRC Handbook.

In one embodiment, there is provided a process for separating diene from a feed mixture comprising the diene and at least one other unsaturated hydrocarbon compound, where the process comprises contacting the mixture with a diene-selective adsorbent which is an ion-exchanged zeolite. Desirably, the ion-exchanged zeolite is a Y zeolite, X zeolite, and/or low silica X zeolite, (LSX). Most desirably, the exchangeable cationic sites of the zeolite are ion-exchanged with silver cation or copper cation. It is preferred that the zeolite be a silver zeolite (Ag-zeolite). The character of these zeolites will be described more particularly below. In the case of type LSX zeolite, it is preferred that it have a silicon to aluminum atomic ratio of less than 1.2. It is most preferred that the ratio of Si/Al be about 1.

It is desirable that at least some of the ion exchange sites of the zeolites contain the silver cation in the case of Ag-zeolite. In alternate embodiments, in the case of Ag-zeolite, a majority, and/or substantially all, of the cation sites are occupied by silver in a +1 oxidation state (+1 valence state). In the case of Cu-zeolite, it is also desirable that at least some of the ion exchange sites contain copper ions. In alternate embodiments, a majority, and/or substantially all, of the sites are

ion exchanged with copper, in the case of copper exchanged zeolites where the copper is in the +1 valence or oxidation state.

In another embodiment, the invention provides a process for causing the separation of diene from one or more other unsaturated hydrocarbons, particularly mono-olefin as described above, using a type A zeolite. In this process the diene is separated from a feed mixture utilizing the type A zeolite having an alkali-metal cation or an alkaline earth metal cation at respective exchangeable cationic sites to cause the selective adsorption of the diene.

Desirably, commercially available 5A zeolite is used. The 5A zeolite contains calcium (Ca) as the major cation. This means that for all the available cation sites of A-zeolite, Ca is found at over half such sites. The minor cation is sodium. Therefore, the 5A zeolite has substantially and essentially all of its cationic sites occupied by Ca and Na, but primarily Ca. This 5A zeolite is also referred to herein as CaA zeolite.

In one embodiment, the type A zeolite optionally contains a mixture of cations besides the alkali metal and alkaline earth metal. Therefore, at some of the cation exchange sites of the zeolite, cations other than +1 and +2 will be present. The nominal formula of this zeolite is $M^{+1}_x Z^{+2}_y A^{+3}_b [(AlO_2)_{12} (SiO_2)_{12}]$ wherein the value of x is 0 to 12 and the value of y is 0 to 6, and the value of b is at minimum zero and at maximum less than the sum of x plus y, provided that: $x + 2y + 3b$ is 12. This is believed to provide a mixture of cations in this type A zeolite which is balanced. It is preferred that when the A zeolite contains tri-valent (+3) cations, the atomic amount of such tri-valent is less than the combined amount of the alkali and alkaline metal cations. It is most preferred that in the aforesaid nominal general formula, the alkaline earth metal is primarily Ca, providing Ca-A (5A) zeolite.

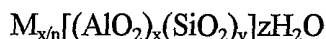
The method and adsorbents (sorbents) of the invention are particularly suited for temperature swing adsorption (TSA) and pressure swing adsorption (PSA). The process is effective to separate diene from a mixture containing one or more other unsaturated hydrocarbons and particularly mono-olefin compounds. Before further describing the invention and the use of zeolites of the invention in TSA and

PSA processes, more particular description of the physical characteristics of the zeolites of the invention is provided along with preferred ion exchange method.

Zeolites have historically been used as adsorbents due their selectivity. Zeolites selectively adsorb molecules on the basis of the size and the shape of the adsorbate molecule and are therefore called molecular sieves. Zeolites have been known for use in selective adsorption of carbon monoxide and hydrocarbons. Crystalline zeolite Y, zeolite A and zeolite X are described in U.S. Patent Nos. 3,130,007; 2,882,243; 3,992,471 and 2,882,244; each of which is incorporated by reference in its entirety. Type 5A zeolite, and type 13X zeolite are described for nitrogen adsorption in U.S. Patent No. 5,551,257. Types 4A (Na-A) and 5A (Ca-A) zeolites, are described in U.S. Patent No. 3,785,122. Low silica X zeolite (LSX) having Si/Al ratio less than or equal to 1.25, desirably less than or equal to 1.2, and preferably about 1 is described in U.S. Patent No. 5,268,023. Each of the aforementioned patents is incorporated herein by reference in its entirety.

Consistent with the features described in these patents, zeolite characteristics are below excerpted from "Gas Separation Processes" by R.T. Yang (1987, Butterworth Publishers).

Zeolites are crystalline aluminosilicates of alkali or alkali earth elements such as sodium, potassium, and calcium, represented by the stoichiometry:



where x and y are integers with y/x equal to or greater than 1, n is the valence of cation M, and z is the number of water molecules in each *unit cell*. Unit cells are shown in **Figures 41(B) and 41(C)**. The cations are necessary to balance the electrical charge of the aluminum atoms, each having a net charge of -1. The water molecules can be removed with ease upon heat and evacuation, leaving an almost unaltered aluminosilicate skeleton with a void fraction between 0.2 and 0.5. The skeleton has a regular structure of cages, which are usually interconnected by six windows in each cage. The cages can imbibe or occlude large amounts of guest molecules in place of water. The size of the window apertures, which can be

controlled by fixing the type and number of cations, ranges from 3 Å to 10 Å. The sorption may occur with great selectivity because of the size of the aperture (and to a lesser extent because of the surface property in the cages) - hence the name *molecular sieve*.

5 At least forty species of naturally occurring zeolites have been found. The principal ones are chabazite, $(\text{Ca}, \text{Na}_2) \text{Al}_2\text{Si}_4\text{O}_{12}(6 \text{ H}_2\text{O})$; gmelinite; $(\text{Na}_2, \text{Ca}) \text{Al}_2\text{Si}_4\text{O}_{12}(6 \text{ H}_2\text{O})$; mordenite, $(\text{Ca}, \text{K}_2, \text{Na}_2), \text{Al}_2\text{Si}_{10}\text{O}_{24}(6.66 \text{ H}_2\text{O})$; levynite, $\text{CaAl}_2\text{Si}_3\text{O}_{10}(5 \text{ H}_2\text{O})$; and faujasite, $(\text{Na}_2, \text{Ca}, \text{Mg}, \text{K}_2)\text{OAl}_2\text{Si}_{4.5}\text{O}_{12}(7 \text{ H}_2\text{O})$. More than 150 types of zeolites have been synthesized; they are designated by a letter or
10 group of letters - Type A, Type X, Type Y, Type ZSM, and so on. The commercial production of synthetic zeolites started with the successful development of low-temperature (25-100°C) synthesis methods using very reactive materials such as freshly coprecipitated gels or amorphous solids.

 The primary structural units of zeolites are the tetrahedra of silicon
15 and aluminum, SiO_4 and AlO_4 . These units are assembled into secondary polyhedral building units such as cubes, hexagonal prisms, octahedra, and truncated octahedra. The silicon and aluminum atoms, located at the corners of the polyhedra, are joined by a shared oxygen. The final zeolite structure consists of assemblages of the secondary units in a regular three- dimensional crystalline framework. The ratio
20 Si/Al is commonly one to five. The aluminum atom can be removed and replaced by silicon in some zeolites, thereby reducing the number of cations; and the cations can also be exchanged. The inner atoms in the windows are oxygen. The size of the windows depends, then, on the number of oxygen atoms in the ring - four, five, six, eight, ten, or twelve. The aperture size, as well as the absorptive properties, can be
25 further modified by the number and type of exchanged cations. A description of the structures will be given only for the zeolites important in gas separation, Type A and Type X and Y. (See Table I).

 Type A. The structural unit in Type A zeolite, as well as in Types X and Y, is the truncated octahedron, shown in **Figure 41(A)**. This unit is also called
30 sodalite cage, as sodalite is formed by directly fusing the four-member rings of the

units. The four-member rings of the sodalite units can also be linked through four-member prisms, as shown in **Figure 41(B)**, which is type A zeolite. The unit cell of Type A zeolite, as shown in this figure, contains 24 tetrahedra, 12 AlO_4 and 12 SiO_4 . When fully hydrated, 27 water molecules are contained in the central cage or cavity of the unit cell, and in the eight smaller sodalite cages. The free diameter in the central cavity is 11.4 Å, which is entered through six eight-member oxygen-ring apertures with a minimum diameter of 4.4 Å. There are twelve negative charges to be balanced by cations in each unit cell. The most probable locations for the cations are indicated in **Figure 41(D)**. Type I is at the center of the six-member ring, thus at one of the eight corners of the cavity. Type II is at the eight-member aperture, directly obstructing the entrance. Type III is near the four-member ring inside the cavity. Type A zeolites are synthesized in the sodium form, with 12 sodium cations occupying all eight sites in I and three sites in II, plus one site in III. This is the commercial Type 4A zeolite, with an effective aperture size of 3.8 Å. The sodium form can be replaced by various other cations or by a hydrogen ion. The commercial Type 3A zeolite is formed by exchanging Na^+ with K^+ , resulting in a smaller effective aperture size due to the larger K^+ . The aperture size of the sodium form can also be increased by exchanging Na^+ with Ca^{+2} or Mg^{+2} , since 2 Na^+ are replaced by one bivalent cation. The form of the exchanged Ca^{+2} or Mg^{+2} is Type 5A with rather unobstructed and larger apertures.

Types X and Y. The skeletal structure of Types X and Y zeolites are the same as that of the naturally occurring faujasite. The sodalite units are linked through six-member prisms, as shown in the unit cell in **Figure 41(C)**. Each unit cell contains 192 (Si, Al) O_4 tetrahedra. The number of the aluminum ions per unit cell varies from 96 to 77 for Type X zeolite, and from 76 to 48 for Type Y zeolite. This framework has the largest central cavity volume of any known zeolite, amounting to about 50% void fraction in the dehydrated form. A unit cell, when fully hydrated, contains approximately 235 water molecules, mostly in the center cavity. The aperture is formed by the twelve-member oxygen rings with a free diameter of approximately 7.4 Å. Three major locations for the cations are indicated in **Figure**

41(E). The locations are: center of the six-member prism (I) and opposite to I in the sodalite cage (I'); similar to I and I' but further from the central cavity (II and II'); and at the twelve-member aperture (III and III'). The commercial 10X zeolite contains Ca^{+2} as the major cation, and Na^{+} is the major cation for 13X zeolite. The distribution of Na^{+} , K^{+} , Ca^{+2} , other cations, and H_2O in X and Y zeolites. The BET surface area measured with N_2 for zeolites falls in the range between 500 and 800 m^2/g .

In one aspect, adsorbents of the invention, as described below, achieve selective adsorption by means of the π -complexation mechanism. Separation by π -complexation is a subgroup of chemical complexation where the mixture is contacted with a second phase, which contains a complexing agent. The advantage of chemical complexation is that the bonds formed are stronger than those by van der Waals forces alone, so it is possible to achieve high selectivity and high capacity for the component to be bound. At the same time, the bonds are still weak enough to be broken by using simple engineering operations such as raising the temperature or decreasing the pressure.

The π -complexation generally pertains to the main group (or d-block) transition metals, that is, from Sc to Cu, Y to Ag, and La to Au in the periodic table. These metals or their ions can form the normal σ bond to carbon and, in addition, the unique characteristics of the d orbitals in these metals or ions can form bonds with the unsaturated hydrocarbons (olefins) in a nonclassic manner. This type of bonding is broadly referred to as π -complexation, and has been considered for gaseous hydrocarbon separation and purification using cumbersome liquid solutions.

It is known, that for many olefin separations, conventional π -complexation sorbents did not provide a large working capacity for the target olefin. The examples below show that the sorbents of the invention have superior selectivity for 1,3-butadiene adsorption. The examples show the new adsorbents (sorbents) usable with preferred PSA and TSA processes for very effective diene separation.

The PSA process is effectively usable with the new sorbents of the invention. Here, multiplicity of periodic steady states is an important aspect of cyclic

adsorption process. For pressure swing adsorption (PSA), multiple steady states exist for a fixed set of operating conditions, over a particular range of one or more of these operating variables (i.e., bifurcation variables). The final stable state depends only on the initial condition (i.e., the perturbation variables).

5 There are a variety of commercial applications in which component separation is conducted by pressure swing adsorption (PSA) and temperature swing adsorption (TSA). Other less commonly used processes are volume swing adsorption and concentration swing adsorption. The most commonly described are PSA and TSA systems.

10 In PSA processing, a feed mixture containing a more readily adsorbable component and a less readily adsorbable component is passed through an adsorbent bed capable of selectively adsorbing the more readily adsorbed component at an upper adsorption pressure. The less readily adsorbable component passes through the bed and is recovered from the discharge end of the bed. Then, the bed is
15 depressurized to a lower desorption pressure for desorption of the more readily adsorbable component, and its removal from the bed. Thereafter, the cyclic operation resumes.

 In temperature swing adsorption processing, the adsorbent is exposed to the feed mixture for a period of time during which the more readily adsorbed
20 component is adsorbed. Thereafter the flow of the feed is shut off from the adsorbent bed and the adsorbent is exposed to a purge fluid, typically a gas, which strips the adsorbed component from the bed and regenerates the bed for further use. In TSA, the adsorbed component is driven off from the bed by heating the adsorbent in the regeneration state. Therefore, the temperature of desorption is higher than the
25 temperature of the adsorption portion of the cycle. Details of PSA and TSA adsorption will not be repeated here, as they may be found in the following United States Patents, each of which is incorporated by reference herein, in its entirety: 5,268,023; 5,551,257; 5,554,208; 5,672,196; 5,672,196.

 Ion exchange of zeolite is easily accomplished by mixing the zeolite
30 in an aqueous solution of the metal salt. The metal of the salt is the metal to be

exchanged into the cationic site. The concentration of the solution is varied according to the desired level of ion exchange. The ion exchanged zeolite is then removed by filtration from the aqueous solution and washed free of the soluble salts. This batch ion exchange is widely used due to its simplicity. Essentially complete ion exchange
5 can be achieved by repeating the same procedure several times. By such repeated treatment, over 90% of the exchangeable cationic sites are ion-exchanged with Ag^+ . Preferably, over 95% of such sites are ion exchanged. The same high level of exchange is obtainable with the copper ion exchange. The Ag zeolites of the invention were prepared by ion exchanging with a solution of AgNO_3 containing five
10 times the cationic exchange capacity of the zeolites. This was done to assure complete ion exchange. The Cu-zeolites of the invention were prepared by ion exchanging with a solution of CuCl_2 or $\text{Cu}(\text{NO}_3)_2$, followed by reduction of Cu^{+2} to Cu^{+1} .

The following examples show new sorbents for the challenging
15 separation of removing trace amounts of dienes (50 PPM) from a normal alpha olefin (NAO) stream. The sorbents of the examples below demonstrate operability for a pressure swing adsorption (PSA) or temperature swing adsorption (TSA) mode.

The sorbents of the example were pre-selected based on two types of interactions: kinetic and weak chemical complexation. The first type of interaction
20 derives from the molecular sieving effects of certain substrates such as zeolites or carbon molecular sieves (CMS). However, zeolites were mainly considered for this application due to their high Henry's Law region adsorption. For this approach, the small differences in the kinetic diameters of mono-olefin are exploited. This is accomplished by exchanging cations of various sizes into the pore aperture of type A
25 zeolite.

Due to the olefinic nature of the components involved in the examples, weak chemical and complexation-based sorbents that have demonstrated the capabilities of adsorbing olefin over paraffins are not necessarily suited for diene separation from mono-olefin. In the separation of diene from mono-olefin, both
30 adsorbates are olefinic in character. Dienes are known to have three arrangements of

the double bonds. Double bonds that alternate with single bonds are said to be conjugated; double bonds that are separated by more than one single bond are said to be isolated. A third, less important class of dienes contain cumulated double bonds, that is, double bonds adjacent one another and known as allenes. One of the most common dienes is 1,3-butadiene. Its boiling point is -4.4°C and very close to 1-butene (-6.3°C). Separation of these two compounds is very difficult due to their close boiling points. The major difference between the two is the conjugate diene nature of 1,3-butadiene. Since 1,3 butadiene is present in such low concentrations, the bond between the sorbate and the adsorbent must be very strong in order to adsorb significant amounts of butadiene at such low partial pressures.

In the examples, it was shown that the properties of the sorbent can be tailored by selecting specific cations and substrates. When dealing with bulk separations, high amounts adsorbed at low pressures are usually not desired, and are usually avoided because they limit the working capacity of the adsorbent. However, for this particular application, a high Henry's law constant is required. Therefore, zeolite-based sorbents are a good candidate for substrates. It is shown that Ag^{+} exchange Y zeolite has high affinity for olefins at very low pressures. Therefore, the examples focus on using zeolitic materials such as Type A, X, or Y, ion exchange with Cu^{+} or Ag^{+} cations to carry out the separation of 1, 3-butadiene from 1-butene. It should be noted that the separation of the conjugated butadiene from butene is merely exemplary. The processes described below are also applicable to separate other dienes such as hexadiene and octadiene from mixtures containing hexene and octene. The temperatures and pressure given below are also exemplary.

Depending on the chosen conditions, the separation is accomplished in the gas phase, the liquid phase or some combination thereof, including for example, saturated gas. It should be noted that the butadiene and butene of the examples share common chemical characteristics with other diene/mono-olefin combinations described earlier. Therefore, the effectiveness of the invention in separating all such stated combinations is apparent.

The sorbents described in the examples below contained various cations included in high surface area substrates. The dispersion of cations was accomplished using ion exchange. The chemistry of ion exchange in zeolites is well documented. See USPN 2,882,243, 2,882,244 and 5,268,023, each of which is incorporated herein in its entirety. All exchanges were performed similarly. They involved vacuum filtering and washing of the zeolite with deionized water. Compared to the original cation exchange capacity (CEC), each solution contained 10-fold cation equivalents. This procedure ensured 100% exchange. For A (Linde), LSX (low silica X, UOP), and Y (Strem Chemicals) zeolites, the starting forms contain Na^+ . The zeolites used were powder form (binderless). Prior to use the samples were calcined in vacuo at 350°C .

In the examples below, the hydrocarbons used as the adsorbates were 1,3 butadiene (CP grade, Matheson), 1-butene (CP grade) and helium (pre-purified grade, Metro Welding 99.995 %) was used as the carrier gas and as the regeneration gas. The gasses were used without further purification. Isotherms and uptake rates were measured utilizing both a Shimadzu TGA-50 microbalance system following well known procedures. For low pressure data (<0.05 atm), a Micromeritics ASAP 2010 pore size distribution analyzer was utilized. This system is capable of accurately measuring pressures in a range between 1×10^{-7} - 1.25 atm. While one can obtain data at very low pressures with the Micromeritics ASAP 2010, this is very time consuming. The Shimadzu TGA-50 thermogravimetric analyzer is used to screen potential sorbents. Also, measurements were made at two temperatures (25°C , 70°C) in order to obtain isosteric heats of adsorption. The overall diffusion time constants, D/R^2 , were calculated from the uptake curves measured from a stepped pressure increment from 0. to 0.6 atm by well known methods and assumptions.

FURTHER EXAMPLES

Example 5

Pre-screening of Y-type Zeolites for 1,3-Butadiene Selectivity

The framework structure of LSX and Y-type zeolites resembled that of the naturally occurring faujasite (see **Figure 41**). The pores of these zeolites are made of 12-member oxygen rings. They have an aperture size of about 8.1 Å. They only differ in the ratios of Si/Al. This ratio determines the number of cations per unit cell and therefore has a significant effect on the adsorption properties. Y-type zeolites contain between 56 and 76 cation sites, respectively. It is because of the properties mentioned above that these zeolites were selected as substrates. The large size aperture facilitates the diffusion of large molecules such as 1,3-butadiene and 1-butene. Also, the large number of cation sites available for exchange with Cu^{1+} or Ag^{1+} helps increase the adsorption capacity.

The pure-component equilibrium isotherms of 1,3- C_4H_6 and 1- C_4H_8 on NaY and NaLSX type zeolites at 70°C are shown in **Figure 42**. The partial pressures ranged from .06 to 1 atm. While these pressures are outside the range of interest for 1,3- C_4H_6 , they are useful for screening potential substrates and for determining capacities for 1- C_4H_8 . The equilibrium data was fitted with the Langmuir isotherm model. The equilibrium amounts of 1,3- C_4H_6 and 1- C_4H_8 adsorbed at 70°C at 1 atm on NaY zeolite were 2.80 and 2.69 mmol/g respectively. This equals about 36 molecules of 1,3- C_4H_6 and 34 molecules of 1- C_4H_8 per unit cell of NaY-type zeolite. Uptake curves for 1,3- C_4H_6 and 1- C_4H_8 on NaY-type zeolites are shown in **Figure 43**. They were obtained by performing a step change in pressure from 0-0.06 atm. Both components diffused very fast. Complete uptake was achieved within 50 seconds. This was due to the very large pore aperture size of the NaY zeolite, about 7.4 Å. Diffusion time constants, D/R^2 , were calculated by fitting experimental data with the solution of the diffusion equation for spherical particles as described by Kärger and Ruthven in 1992. The values of D/R^2 obtained for 1,3- C_4H_6 and 1- C_4H_8 at 70°C were 7.85×10^3 and 5.76×10^3 1/s, respectively. The ratio of the diffusivities is rather small (≈ 1.3) for kinetic separation application. However, one favorable characteristic of Y-type zeolite is its relatively high Henry's Law constant. This indicates that the Y-type zeolites have good affinity for C4's and are also good candidates for C6's and C8's.

Example 6**Selectivity of Ion-Exchanged Y-Zeolite for 1,3-Butadiene**

As per Example 5, Y-type zeolites have a very high affinity for C4's at low pressures. Therefore, this material is a good substrate for 1-butene purification, and also for hexene and octene purification. In order to increase the affinity of the NaY zeolite for 1,3 butadiene, the Na¹⁺ cation was fully exchanged by Ag¹⁺ which is capable of π -complexation with olefinic compounds. The pure component equilibrium isotherms for 1,3-C₄H₆ and 1-C₄H₈ AgY zeolite at 70°C and 25°C are shown in **Figure 44**. The partial pressure in this isotherm ranged from 1×10^{-5} atm to 1 atm. The lower end of the scale corresponds to a concentration equal to 10 PPM. The equilibrium amounts of 1,3-C₄H₆ and 1-C₄H₈ at 70°C and 1 atm were measured at 2.8 and 2.3 mmol/g. These results are very interesting because at high loadings it appears that exchanging Na with Ag had lesser effect on the amounts of 1,3-C₄H₈ adsorbed.

Low pressure 1,3-C₄H₆ and 1-C₄H₈ adsorption data on AgY type zeolite at 70°C is also shown in **Figure 44**. In this Figure, it can be observed that at 70°C the amount of 1,3-C₄H₆ adsorbed at 50 PPM was about 0.5 mmol/g. This amount is somewhat small. The amount of 1,3-C₄H₆ is improved by decreasing the adsorption temperature or increasing pressure. Equilibrium adsorption isotherms for 1,3-C₄H₆ on AgY type zeolite are shown in **Figure 44** also. Although 1,3-C₄H₆ adsorption did not improve in the region of importance, 1×10^{-5} to 5×10^{-5} (10-50 PPM), there was an increase in adsorption at higher loadings.

The lack of 1,3-C₄H₆ adsorbed in the low pressure regime with the decrease in temperature could be attributed to equipment error. It is possible for the Micromeritics ASAP 2010 to cut off adsorption before uptake completion for a particular pressure point if the system is too slow diffusing. This possible error was corrected and a new equilibrium isotherm for 1,3-C₄H₆ on AgY zeolite was included as per an example which follows below.

Example 7**Confirmation of Selectivity**

In order to confirm the π -complexation activity of the sorbent, it was tested with C_2H_4 at $70^\circ C$. The equilibrium isotherms of C_2H_4 on NaY and AgY type zeolites at $70^\circ C$ are shown in **Figure 45**. In this figure, the effect of π -complexation can be clearly observed at low pressures. However, at higher pressures, this effect is somewhat diminished. This phenomenon could be attributed to a filling of the pore cavity of Y-type zeolite. However, for this particular application, the behavior of the sorbent at high loadings is not important. It is the low pressure behavior of the sorbent which is critical for this particular purification-type application.

10 **Example 8**

A-Type Zeolite Selectivity for 1,3-Butadiene

The structural unit of Type A zeolite is the sodalite cage. The unit cell of Type A zeolite contains 12 AlO_4 and 12 SiO_4 (see **Figure 41**). There are twelve negative charges to be balance by cations in each cell unit. The free diameter in the central cavity is 11.4 Å (Yang, 1987). Access to the pores is restricted by 8-membered oxygen rings with a free aperture of 4.3 Å in the unobstructed Ca^{2+} (5A) form. This can be reduced to 3.8 Å by exchanging with Na^+ and to 3.0 Å by exchanging with K^+ . It is this wide variation of pore sizes and smaller cavity size that makes type A zeolites desirable for butadiene separation.

20 Commercially available (5A) Zeolite from Linde was tested. Low pressure equilibrium isotherms for 1,3- C_4H_6 and 1- C_4H_8 on 5A at $25^\circ C$ are shown in **Figure 46**. Equilibrium amounts of 1,3- C_4H_6 and 1- C_4H_8 at 1 atm were measured at 3.8 and 3.3 mmol/g, respectively. The low pressure adsorption of this material was excellent. At a concentration of 50 PPM, this material adsorbed 0.8 mmol/g of 1,3
25 C_4H_6 . The working capacity of this sorbent between 50 and 10 PPM is also excellent. This was measured at approximately 0.7 mmol/g.

Example 9

5A Zeolite and 5A Ion-Exchanged Zeolite Selectivity

This example builds on the success of 5A type zeolite in adsorbing
30 1,3- C_4H_6 at very low loadings. Here, the focus was to reduce 1- C_4H_8 adsorption. As

mentioned earlier, one of the strategies to synthesize a sorbent for this application was to use kinetic or steric effects to separate 1,3-C₄H₆ (butadiene) from 1-C₄H₈ (butene). Therefore, it is possible to limit 1-C₄H₈ adsorption by hindering its uptake or completely excluding it from the pore structure. This was accomplished by exchanging Ca⁺ cations in the pores of Type A zeolite with several cations of various sizes. The pure component equilibrium isotherm for 1,3-C₄H₆ and 1-C₄H₈ on Sr exchanged 5A at 25°C are shown in **Figure 47**. The pressure in this isotherm ranged from 1 x 10⁻⁵ to 1 atm. Equilibrium adsorption amount for 1,3-C₄H₆ on Sr exchanged 5A at 25°C and 1 atm was measured at 3.1 mmol/g. Although this sorbent showed excellent capacity at high loadings (≈ 1 atm), it did not adsorb significant amounts of 1,3-C₄H₆ in the 10-50 PPM regime. Uptake curves for 1,3-C₄H₆ and 1-C₄H₈ on Sr exchanged 5A and 5A were measured at 70°C and are shown in **Figure 47**. The values of D/R² for 1,3-C₄H₆ and 1-C₄H₈ on CaA were calculated at 1.07 x 10² and 7.30 x 10⁻³ 1/s, respectively. Diffusion time constants were also measured on Sr exchanged 5A and were calculated at 8.55 x 10⁻³ and 4.06 x 10⁻³ 1/s, respectively. Due to the larger radius of Sr²⁺ over Ca²⁺ (1.12 vs. 0.99 Å), a small reduction in 1-C₄H₈ uptake rates is observed. However, the reduction in 1-C₄H₈ uptake is not significant enough for a kinetic separation scheme. If the ion exchange is performed with the next larger cation, Ba²⁺, with a radius of 1.34 Å, the uptakes of both adsorbents are severely hindered. Therefore, it is questionable whether hindrance of 1-C₄H₈ access to the pore structure of A type zeolites using simple ion exchange techniques is possible without also blocking 1,3-C₄H₆. The small difference in kinetic diameter between the two molecules is problematic.

Desorption experiments were carried out on 1,3-C₄H₆ on 5A zeolite at 70°C. However, these experiments were performed in the Shimadzu TG-50 TGA. Therefore, they do not include data below 0.06 atm. Equilibrium amounts of 1,3-C₄H₆ on 5A Zeolite at 70°C and 1 atm were measured at 2.81 mmol/g. After desorption, at 1 atm, the sample was exposed to a helium stream at 70°C to regenerate it. However, this procedure only removed 1.23 mmol/g which left 1.58 mmol/g of 1,3-C₄H₆. This final amount was removed by heating the sample to

180°C in the presence of helium. A desorption curve is shown in **Figure 48**. As per the above examples, success has been achieved with 5A zeolite for 1,3-butadiene separation. It is not clear yet the reason for the success of 5A and the lesser performance of Sr exchanged 5A which is very similar structurally. The pore size of this zeolite determines its effectiveness for C6 and C8 separation.

Example 10

1,3 Butadiene/1-Butene Separation: π -Complexation Effects

In previous examples there is shown 1,3-butadiene (C_4H_6) adsorption on AgY zeolite at various temperatures. These examples did not include data to directly compare the effects of π -complexation on C_4H_6 adsorption. This example includes a direct comparison by measuring C_4H_6 adsorption on the sodium-exchanged type Y zeolite (NaY). It is known that the sodium cation is not capable of π -complexating with olefins. A comparison involving AgA and CaA (5A) was not used because of the dominance of kinetic effects in the AgA system. The pore size of AgA lies in the range between 3A and 4A type zeolites.

Equilibrium adsorption isotherms for C_4H_6 on AgY and NaY at 120°C are shown in **Figure 49**. The effect on π -complexation is observed in the equilibrium amounts of C_4H_6 adsorbed on AgY and NaY at 1 atm which were measured at 3.3 and 2.6 mmol/g, respectively. However, the adsorption of C_4H_6 at 50 PPM of saturation pressure of 1-Butene (C_4H_8) at 120°C (1.1×10^{-3} atm) is a more significant parameter. Using this parameter, the effects of π -complexation are more significant. The adsorption amounts of C_4H_6 at 50 PPM on AgY and NaY were measured at 2.7 and 0.3 mmol/g, respectively. The working capacity of the sorbents in the range of 50 to 10 PPM (1.1×10^{-3} - 2.2×10^{-4} atm) was calculated at 2.35 and 0.2 mmol/g, respectively. When the working capacities of the sorbents are calculated, the superior performance of π -complexation sorbents becomes evident.

Example 11

Butadiene-Butene Separation

In the earlier examples, the isotherms of 1-butene and butadiene on 5A zeolite at 25°C were shown. Added isotherms were measured at 70°C. The isotherms are shown in **Figure 50**. The amounts adsorbed are lower at 70°C. More significantly, the heel of the isotherm for butadiene is shifted toward a higher partial pressure. Fortunately, however, the amount adsorbed is quite high at a butadiene partial pressure of 50 ppm of 10 atm (i.e., the saturation pressure of butene at 70°C. The amount is approximately 1 mmol/g. The amount adsorbed at 10 ppm of 10 atm is nearly zero. Hence 5A zeolite is an attractive sorbent for this selective removal of diene at 70°C (at a total pressure of 10 atm). The polar nature of the surface of the zeolite is thought to contribute to the separation.

Table I.

LSX, Y and A zeolite nominal chemical formulas

AgLSX	$\text{Ag}_{96}[(\text{AlO}_2)_{96}(\text{SiO}_2)_{96}]$
AgY	$\text{Ag}_{54}[(\text{AlO}_2)_{54}(\text{SiO}_2)_{138}]$
CaA	$\text{Ca}_6[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}]$
CuLSX	$\text{Cu}_{96}[(\text{AlO}_2)_{96}(\text{SiO}_2)_{96}]$
CuY	$\text{Cu}_{54}[(\text{AlO}_2)_{54}(\text{SiO}_2)_{138}]$
Mixed Metal A	$\text{M}^{+1}_x \text{Z}^{+2}_y \text{A}^{+3}_b [(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}]$ ($x + 2y + 3b = 12$)

Note: In X-type zeolites, the $\text{AlO}_2/\text{SiO}_2$ ratio is greater than 54/138; and the total valence of the cations is equal to the number of AlO_2 units.

The invention provides substantial advantages over conventional methods for separating diene from a mixture. The adsorbents and methods of the invention are useful for purifying mono-olefin from a mixture which includes mono-olefin and diene. The adsorbents and methods can be used to purify either the diene or to purify the mono-olefin. The adsorbents and methods as exemplified in the examples demonstrate particular effectiveness for removing a diene from a mixture comprising the diene and one or more mono-olefins. The

examples show effective separation results using gas-phase separation at the pressures and temperatures stated therein. The adsorbents and processes are demonstrated for a saturated 1-butene (olefin) stream, which is contaminated with 1,3-butadiene (diene), typically at one weight percent or less. The separation in this case may include both gas and liquid phase selective adsorption due to the saturated nature of the 1-butene olefin stream. The processes described herein are described with reference to separation of C4 to C8 diene from a C4 to C8 mono-olefin. The physical characteristics of the adsorbents result in very effective separation as demonstrated by the examples. Depending on the chosen conditions, the separation is accomplished in the gas phase, the liquid phase or some combination thereof, including, for example, saturated gas. For the reasons described above, the adsorbents are also considered to be useful for separation of other dienes, that is C4 to C10 dienes from C4 to C10 mono-olefins. Beyond C10 the process is also thought to be applicable, for example, C12 diene/C12 mono-olefin separation. However, the selectivity and economic benefits are expected to decline for the higher hydrocarbon mono-olefin/diene separation.

The invention provides good results at operating temperatures and pressures that are not extreme. Good results are achievable at pressures on the order of sub-atmospheric (i.e., 0.01 to 0.1 atm) to moderately high (i.e. 20 to 30 atm) and in a pressure swing adsorption method. Good results are achievable at temperatures from ambient or a desired feed temperature (i.e. 0 to 25°C) and up to moderately high (i.e. 250°C), and in a temperature swing adsorption method. With the adsorbents of the invention, temperature swing or pressure swing adsorption processes are usable for effective separation between dienes and mono-olefins. This is demonstrated by the very effective purification of butenes, by removing 1,3-butadiene at concentrations above 20 ppm to final concentration below 10 ppm. Therefore, the invention provides a very attractive solution to the problem of selective adsorption of trace amounts of diene to separate diene from a mixture.

While preferred embodiments of the invention have been described in detail, it will be apparent to those skilled in the art that the disclosed embodiments

may be modified. Therefore, the foregoing description is to be considered exemplary rather than limiting, and the true scope of the invention is that defined in the following claims.

What is claimed is:

- 1 1. A method of separating gaseous alkene selected from the group
2 consisting of ethylene, propylene and mixtures thereof, from a gaseous mixture
3 including the alkene and a sulfur compound, the method comprising the steps of:
4 contacting the gaseous mixture with an adsorbent which preferentially
5 adsorbs the alkene, at a selected temperature and pressure, thereby producing a non-
6 adsorbed component and an alkene-rich adsorbed component; the adsorbent
7 comprising a carrier having a surface area, the carrier having a monolayer of a silver
8 compound or copper compound dispersed on substantially the entire surface area, the
9 silver or copper compound releasably retaining the alkene; and the carrier comprising
10 a plurality of pores having a pore size greater than the effective molecular diameter
11 of the alkene; and
12 changing at least one of the pressure and temperature to thereby
13 release the alkene-rich component from the adsorbent;
14 wherein the adsorbent substantially maintains its adsorbent capacity
15 and preference for the alkene in the presence of the sulfur compound.
- 1 2. The method as defined in claim 1 wherein the monolayer is a
2 silver compound comprising silver nitrate (AgNO_3), and the carrier is silica (SiO_2).
- 1 3. The method as defined in claim 1 wherein the monolayer is a
2 silver compound comprising a silver salt, and wherein the salt is selected from the
3 group consisting of acetate, benzoate, bromate, chlorate, perchlorate, chlorite, citrate,
4 fluoride, nitrate, nitrite, sulfate, and mixtures thereof.
- 1 4. The method as defined in claim 1 wherein the carrier has a BET
2 surface area greater than about 50 square meters per gram and up to about 2,000
3 square meters per gram, and comprises a plurality of pores having a pore size greater
4 than about 3 angstroms and up to about 10 microns.

1 5. The method as defined in claim 1 wherein the carrier is a high
2 surface area support selected from the group consisting of refractory inorganic oxide,
3 molecular sieve, activated carbon, and mixtures thereof.

1 6. The method as defined in claim 5 wherein the refractory inorganic
2 oxide is selected from the group consisting of pillared clay, alumina and silica.

1 7. The method as defined in claim 1 wherein the monolayer is a silver
2 compound comprising a silver (I) halide, and the carrier is silica.

3 8. The method as defined in claim 1 wherein the selected pressure of
4 preferential adsorption is a first pressure, and the pressure of release is a second
5 pressure less than the first pressure, and wherein the first pressure is in a range of
6 about 1 atmosphere to about 35 atmospheres, and further wherein the second pressure
7 is in a range of about 0.01 atm to about 5 atm.

1 9. The method as defined in claim 1 wherein the selected temperature
2 of preferential adsorption is a first temperature, and the temperature of release is a
3 second temperature greater than the first temperature, and wherein the first
4 temperature is in a range of about 0°C to about 50°C, and further wherein the
5 second temperature is in a range of about 70°C to about 200°C.

1 10. The method as defined in claim 1 wherein the retaining of the
2 alkene is accomplished by formation of π -complexation bonds between the silver or
3 copper compound and the alkene.

1 11. The method as defined in claim 1 wherein the monolayer is a
2 copper compound comprising a copper salt, and wherein the salt is selected from the
3 group consisting of bromide, fluoride, iodide, sulfate, and mixtures thereof.

1 12. A sulfur tolerant adsorbent for preferential adsorption of gaseous
2 alkene from a gaseous mixture including the alkene and a sulfur compound, the
3 adsorbent comprising:
4 a carrier; and
5 a silver compound supported on the carrier, wherein the silver
6 compound is a silver salt, and wherein the salt is selected from the group consisting
7 of acetate, benzoate, bromate, chlorate, perchlorate, chlorite, citrate, fluoride, nitrate,
8 nitrite, and sulfate;
9 wherein the carrier has a BET surface area greater than about 50
10 square meters per gram and up to about 2,000 square meters per gram and
11 comprising a plurality of pores having a pore size greater than about 3 angstroms and
12 up to about 10 microns;
13 and wherein the adsorbent substantially maintains its adsorbent
14 capacity and preference for the alkene in the presence of the sulfur compound.

1 13. The adsorbent as defined in claim 12 wherein the adsorbent
2 comprises finely divided particles of silica (SiO_2) with silver nitrate (AgNO_3)
3 dispersed on and supported on the particles.

1 14. The adsorbent as defined in claim 12 wherein the carrier is
2 selected from the group consisting of refractory inorganic oxide, molecular sieve, and
3 activated carbon in particle form.

1 15. The adsorbent as defined in claim 14 wherein the refractory oxide
2 is selected from the group consisting of pillared clay, alumina and silica.

1 16. A method for separating a diene from a mixture including the
2 diene and a sulfur compound, the process comprising the step of:
3 contacting the mixture with an adsorbent which preferentially adsorbs
4 the diene, at a selected temperature and pressure, thereby producing a non-adsorbed

5 component and a diene-rich adsorbed component, wherein the adsorbent comprises
6 an ion-exchanged zeolite selected from the group consisting of zeolite X, zeolite Y,
7 zeolite LSX, and mixtures thereof, the zeolite having exchangeable cationic sites, and
8 a majority of the sites having silver cation or copper cation present, and wherein the
9 preferential adsorption occurs by π -complexation, and further wherein the adsorbent
10 substantially maintains its adsorbent capacity and preference for the diene in the
11 presence of the sulfur compound.

1 17. The method as defined in claim 16 wherein the diene is selected
2 from the group consisting of butadiene, hexadiene, octadiene and mixtures thereof,
3 and wherein the method further comprises the step of changing at least one of the
4 pressure and temperature to thereby release the diene-rich component from the
5 adsorbent.

1 18. The method as defined in claim 16 wherein the diene is 1,3-
2 butadiene, and wherein the mixture includes 1,3-butadiene and at least one other C₄
3 unsaturated compound.

1 19. The method as defined in claim 16 wherein the majority of the
2 cationic sites of the ion-exchanged zeolite contain the silver cation.

1 20. The method as defined in claim 16 wherein the majority of the
2 cationic sites of the ion-exchanged zeolite contain the copper cation.

1 21. The method as defined in claim 16 wherein the mixture comprises
2 at least one mono-olefin having as many carbon atoms as the diene, wherein the
3 diene is selected from the group consisting of butadiene, hexadiene, octadiene, and
4 mixtures thereof; and wherein the mono-olefin is selected from the group consisting
5 of butene, hexene, octene, and mixtures thereof.

1 22. The method as defined in claim 21 wherein the mono-olefin is
2 butene and the diene is butadiene.

1 23. The method as defined in claim 21 wherein the mixture comprises
2 the mono-olefin in a gaseous state and saturated with the diene.

1 24. The method as defined in claim 16 wherein essentially all cationic
2 sites of the ion-exchanged zeolite contain the silver cation.

1 25. The method as defined in claim 17 wherein the selected pressure
2 of preferential adsorption is a first pressure, and the pressure of release is a second
3 pressure less than the first pressure, wherein the first pressure is in a range of about 1
4 atmosphere to about 35 atmospheres, and wherein the second pressure is in a range of
5 about 0.01 atmosphere to about 5 atmospheres.

1 26. The method as defined in claim 17 wherein the selected
2 temperature of preferential adsorption is a first temperature, and the temperature of
3 release is a second temperature greater than the first temperature, wherein the first
4 temperature is in a range of about 0°C to about 150°C, and wherein the second
5 temperature is in a range of about 70°C to about 250°C.

1 27. A method for separating a diene from a mixture including the
2 diene and a sulfur compound, the process comprising the steps of:
3 contacting the mixture with an adsorbent which preferentially adsorbs
4 the diene at a first temperature, thereby producing a non-adsorbed component and a
5 diene-rich adsorbed component, wherein the adsorbent comprises zeolite A having
6 exchangeable cationic sites, a plurality of the zeolite A sites having an alkali metal
7 cation or an alkaline earth metal cation present; and

8 releasing the diene-rich adsorbed component from the adsorbent by
9 elevating the temperature to a second temperature which ranges between about 70°C
10 and about 120°C;
11 wherein the adsorbent substantially maintains its adsorbent capacity
12 and preference for the diene in the presence of the sulfur compound.

1 28. The method as defined in claim 27 wherein the diene is selected
2 from the group consisting of butadiene, hexadiene, octadiene, and mixtures thereof.

1 29. The process as defined in claim 28 wherein a selected pressure of
2 preferential adsorption is a first pressure, and a pressure of release is a second
3 pressure less than the first pressure, wherein the first pressure is in a range of about 1
4 atmosphere to about 35 atmospheres, and wherein the second pressure is in a range of
5 about 0.01 atmosphere to about 5 atmospheres.

1 30. The method as defined in claim 1 wherein the sulfur compound is
2 hydrogen sulfide, and wherein the hydrogen sulfide is present in amounts up to about
3 66 mole%.

1 31. The method as defined in claim 12 wherein the sulfur compound
2 is hydrogen sulfide, and wherein the hydrogen sulfide is present in amounts up to
3 about 66 mole%.

1 32. The method as defined in claim 16 wherein the sulfur compound
2 is hydrogen sulfide, and wherein the hydrogen sulfide is present in amounts up to
3 about 66 mole%.

1 33. The method as defined in claim 27 wherein the sulfur compound
2 is hydrogen sulfide, and wherein the hydrogen sulfide is present in amounts up to
3 about 66 mole%.

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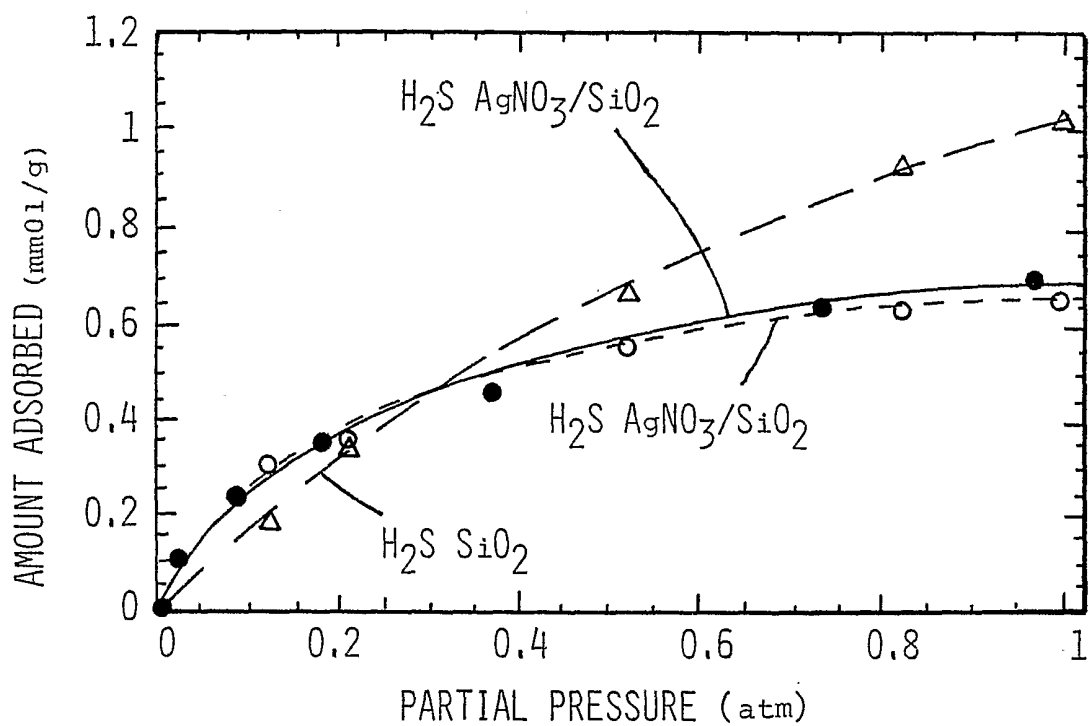


FIG - 1

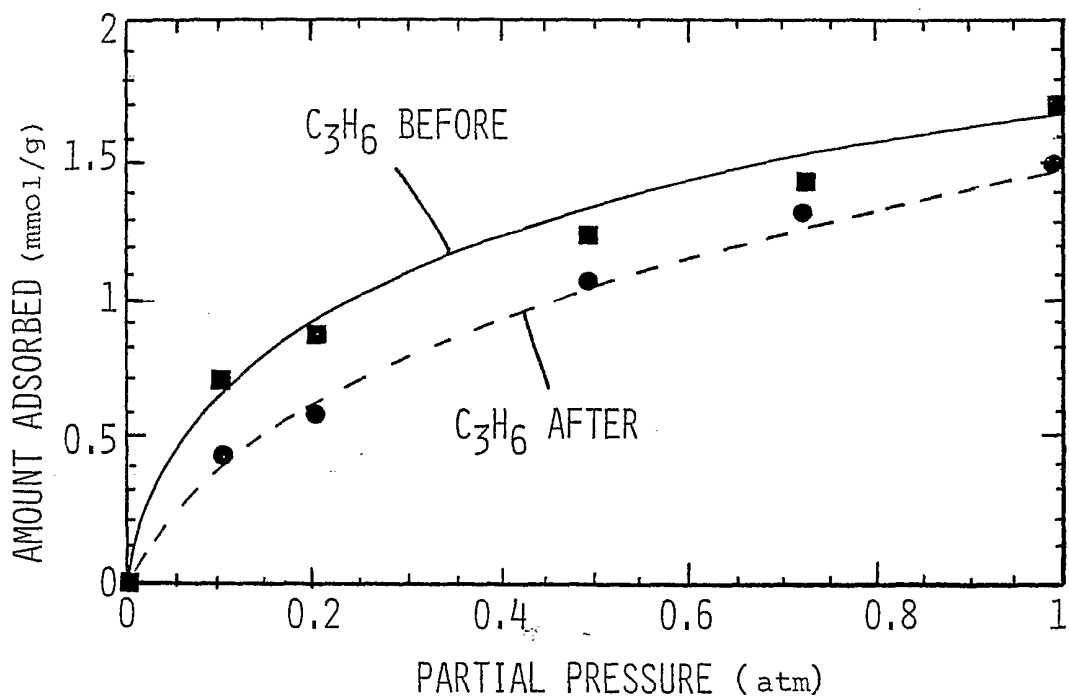


FIG - 2

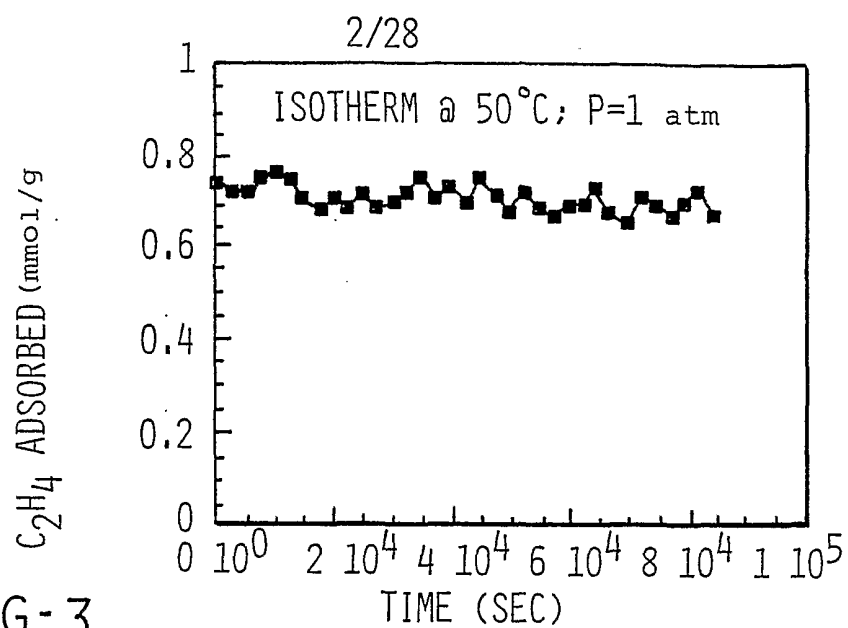


FIG-3

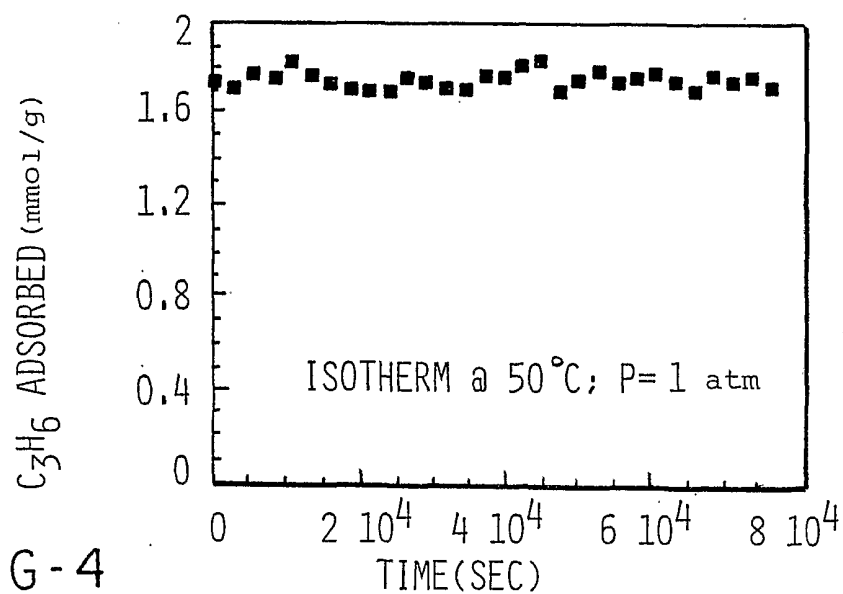


FIG-4

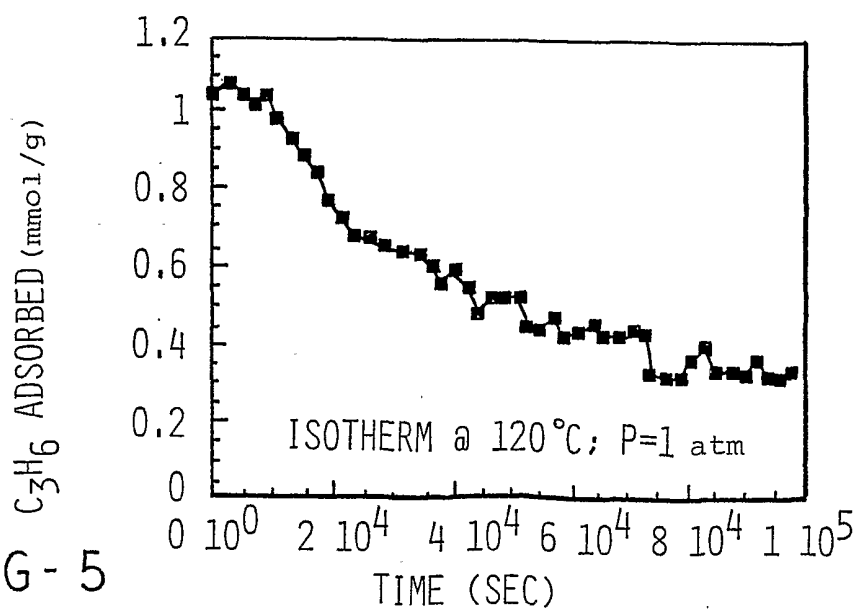


FIG-5

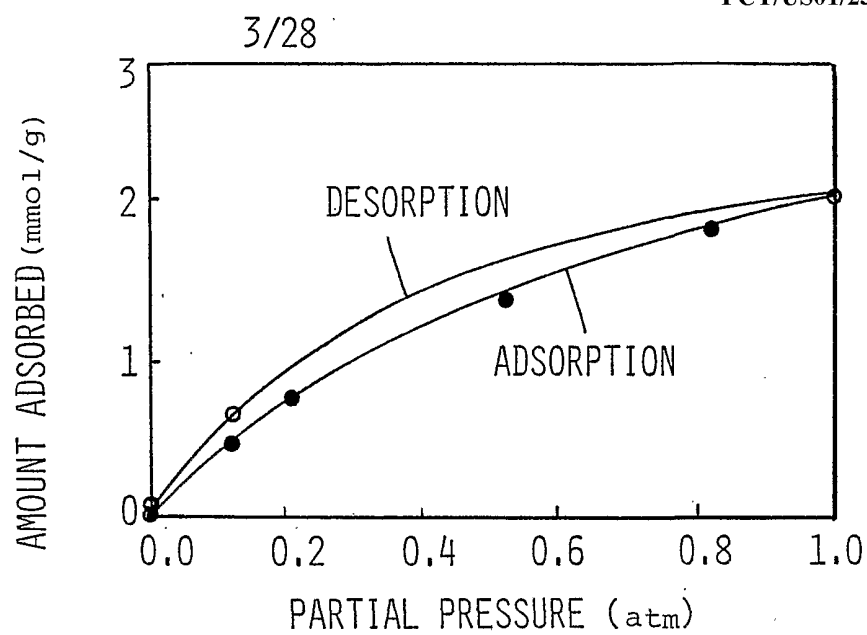


FIG-6

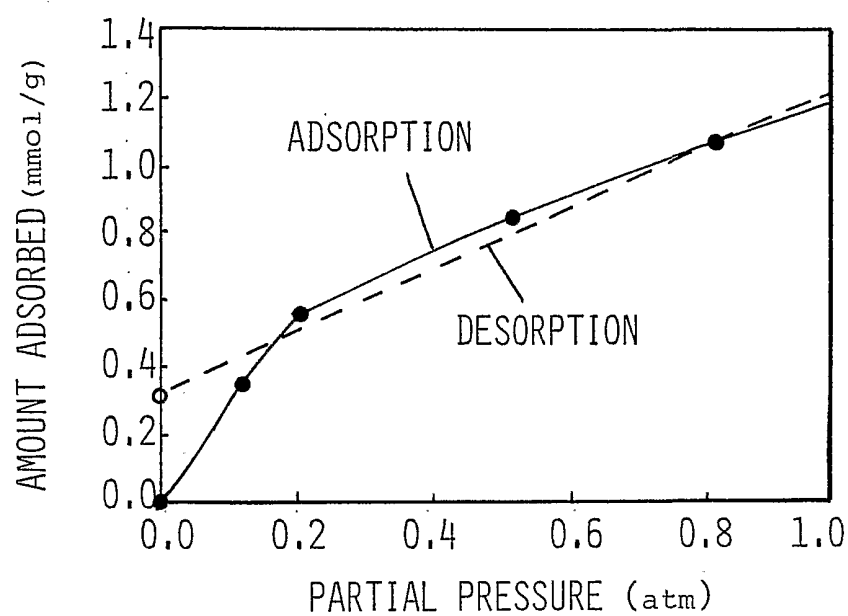


FIG-7

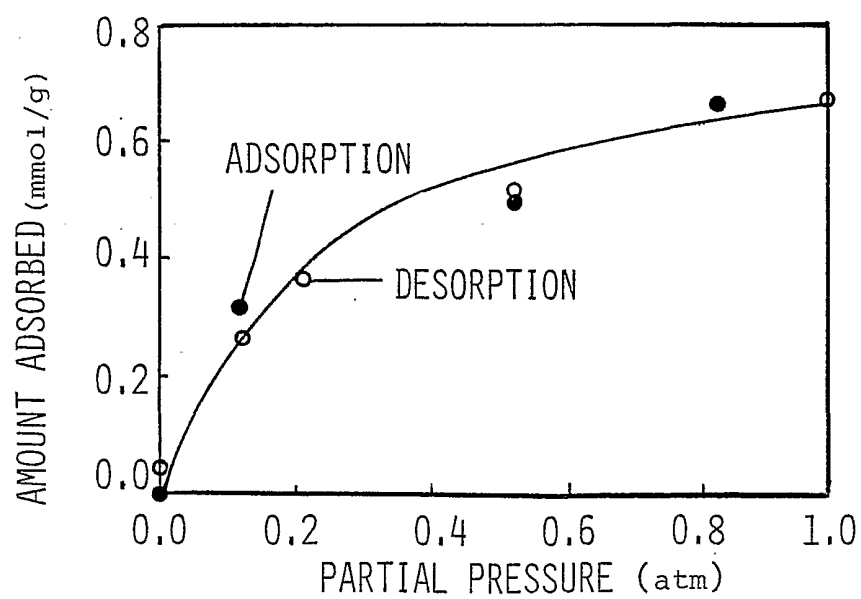


FIG-8

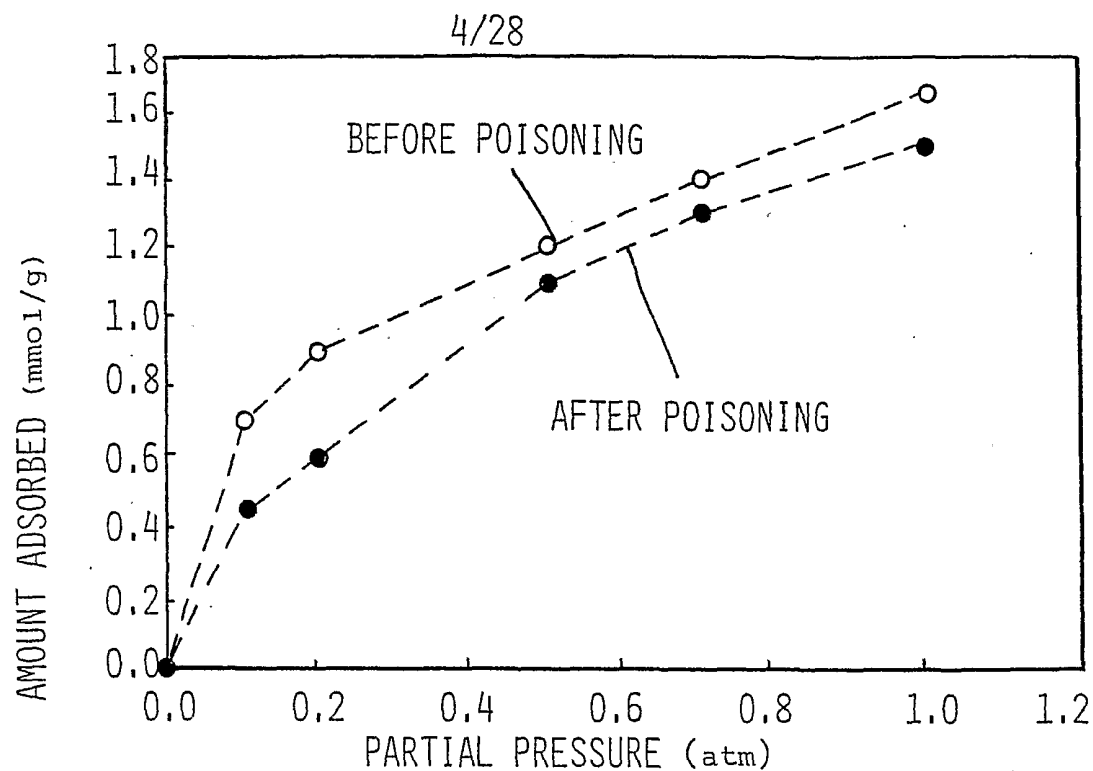


FIG - 9.

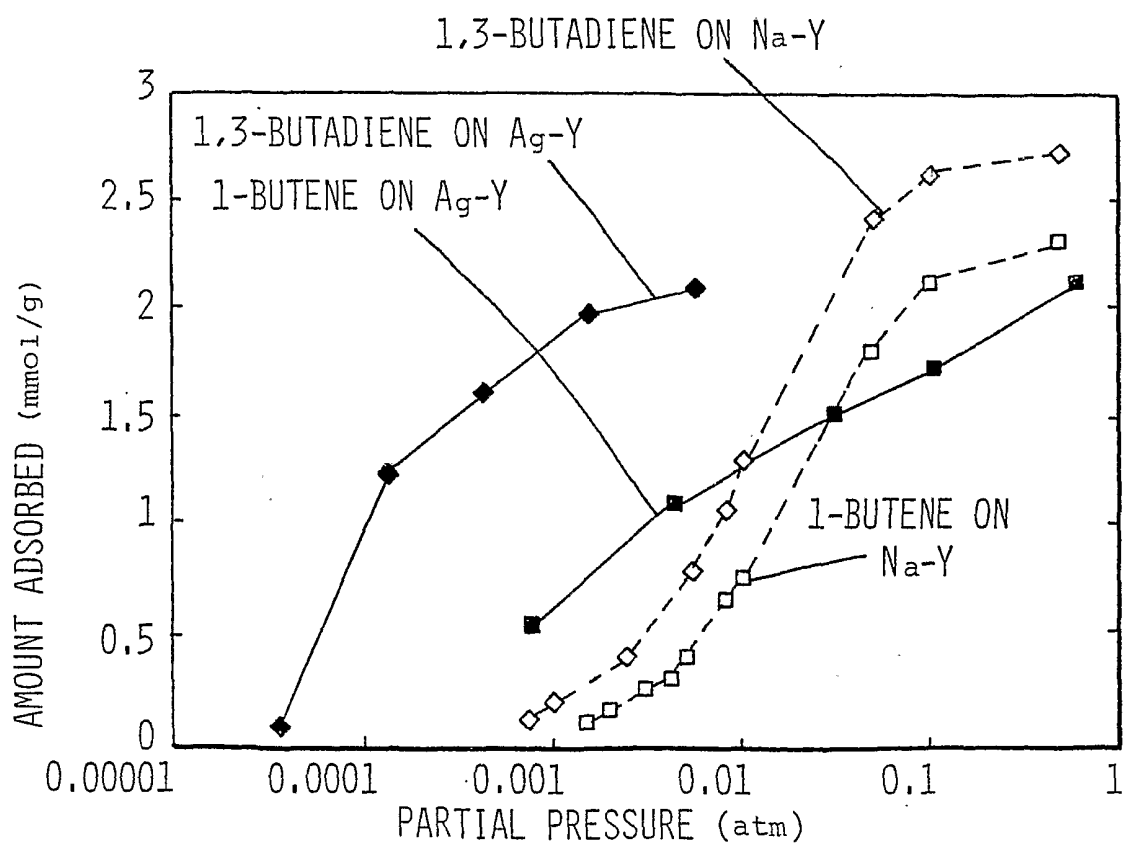


FIG - 11

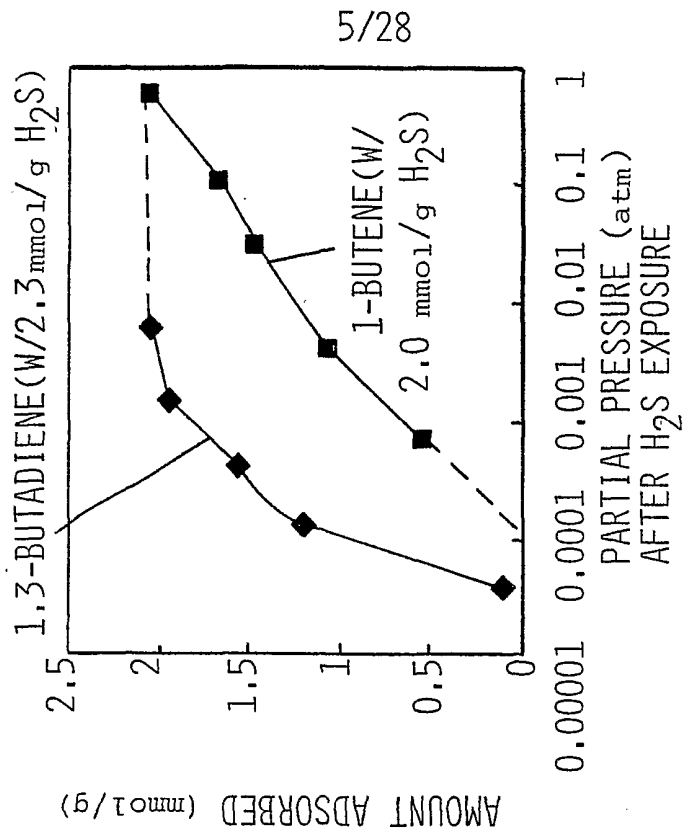


FIG - IOB

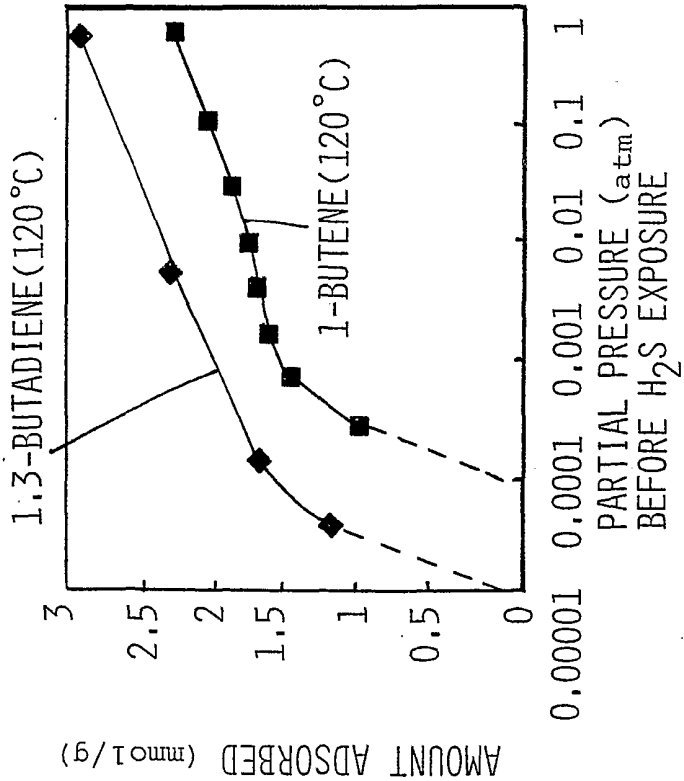


FIG - IOA

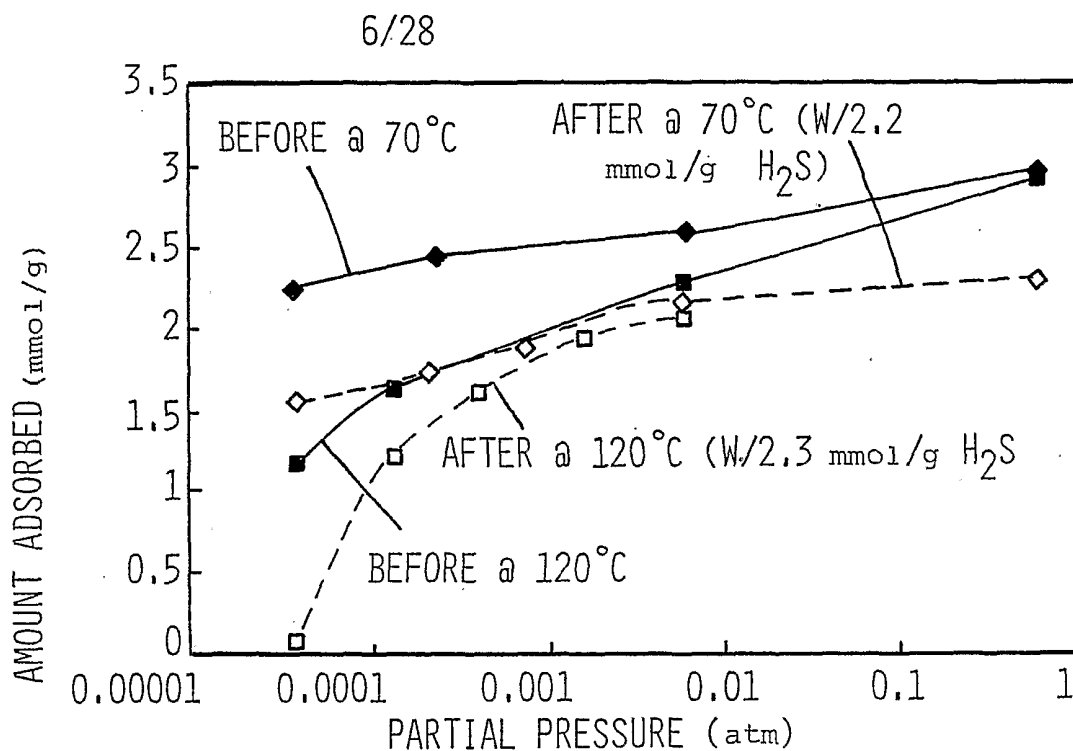


FIG-12A

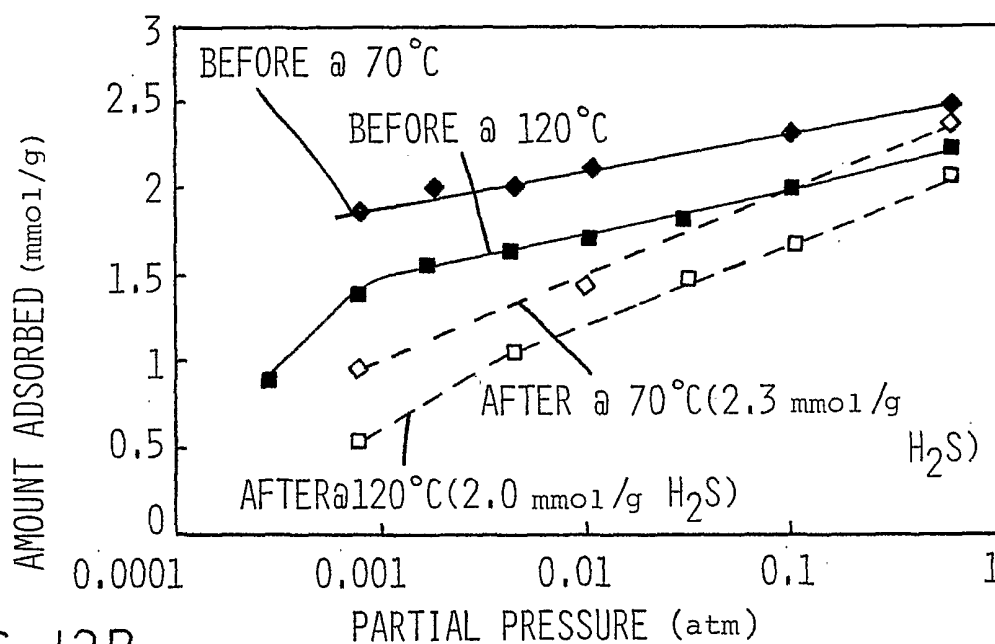


FIG-12B

	1,3-BUTADIENE	1-BUTENE
BEFORE H ₂ S EXPOSURE	24-29 KCAL /mol	16-22 KCAL /mol
AFTER H ₂ S EXPOSURE	7-11 KCAL /mol	6-7 KCAL /mol

FIG-12C

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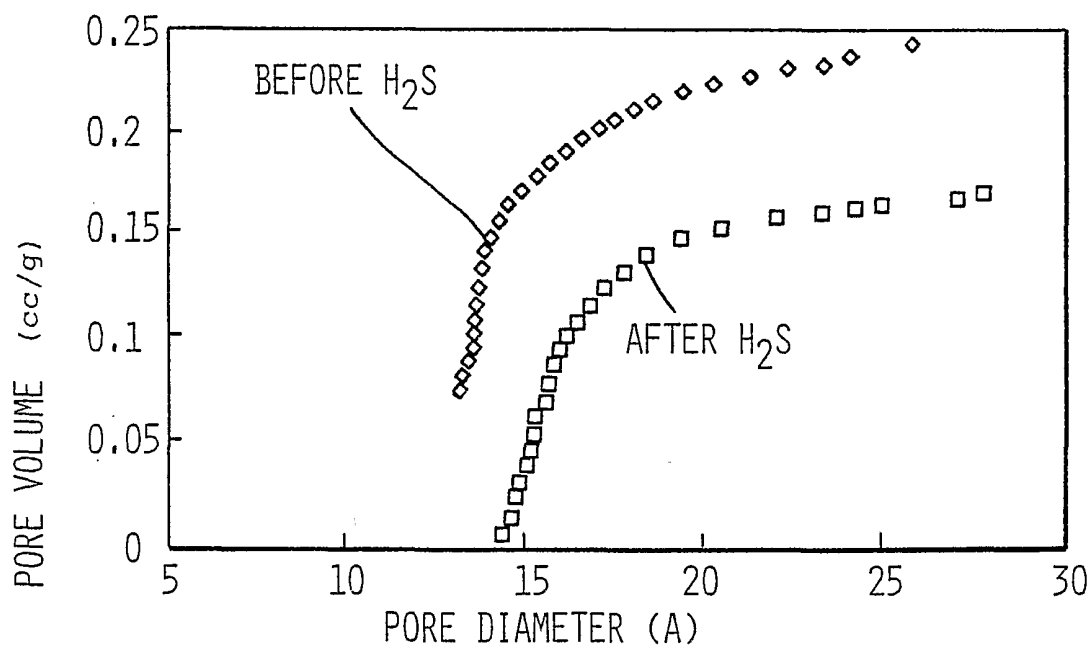


FIG-13

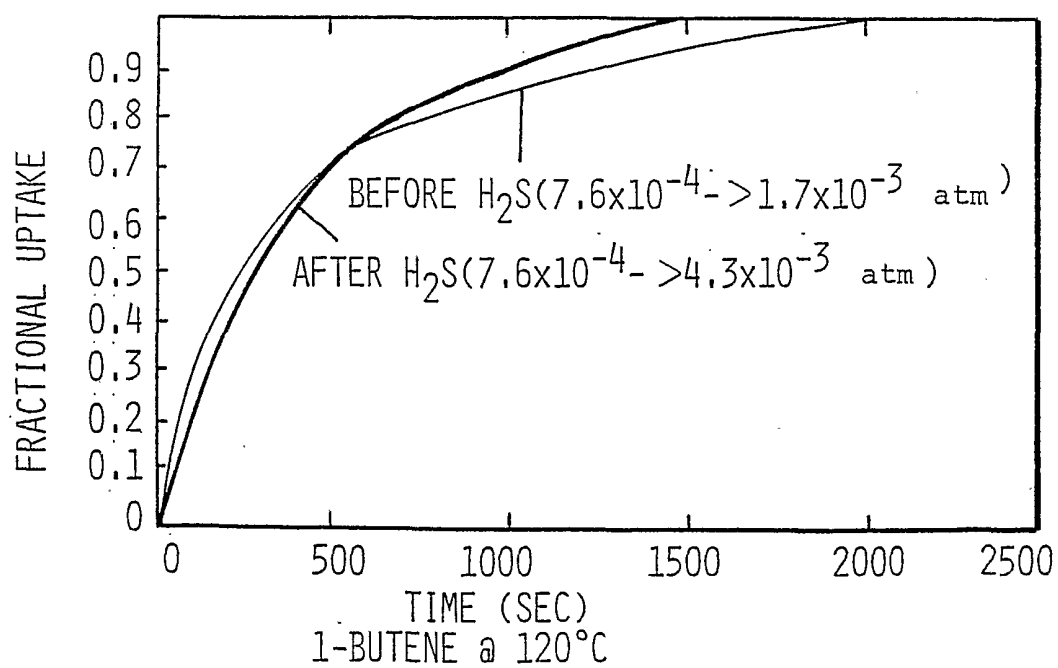


FIG-14A

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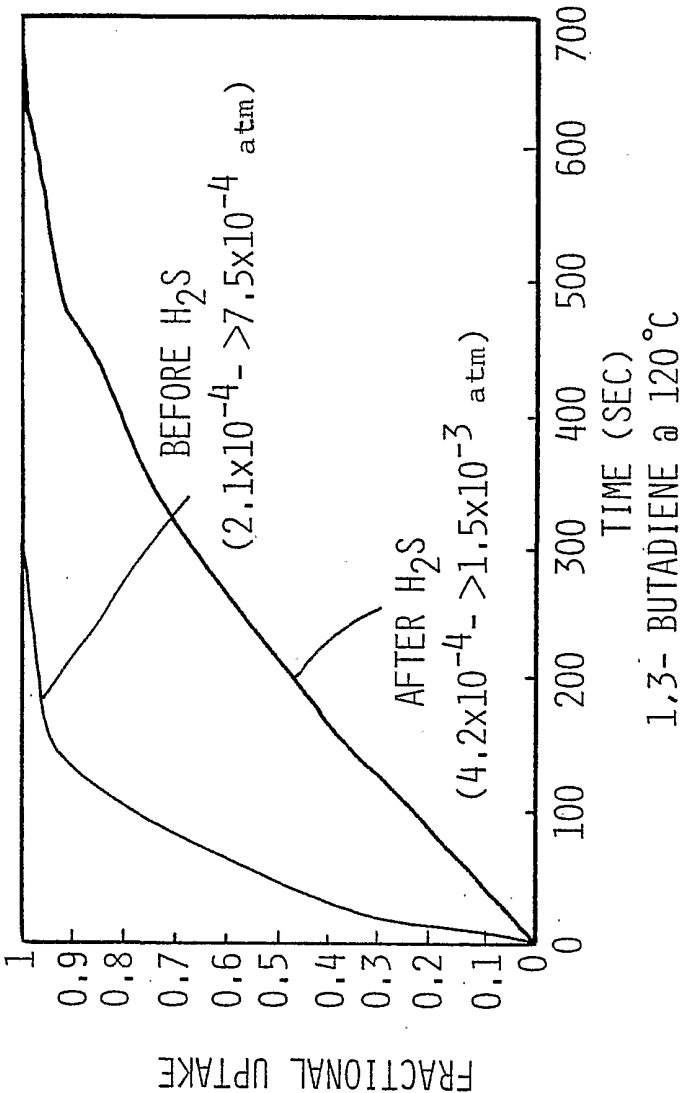


FIG - 14B

FIG - 14C

	BEFORE H ₂ S EXPOSURE	AFTER H ₂ S EXPOSURE
1-BUTENE	1.8x10 ⁻⁴ (7.6x10 ⁻⁴ atm)	1.5x10 ⁻⁴ (7.6x10 ⁻⁴ atm)
1,3 BUTADIENE	8.7x10 ⁻⁴ (2.1x10 ⁻⁴ atm)	2.6x10 ⁻⁴ (4.2x10 ⁻⁴ atm)

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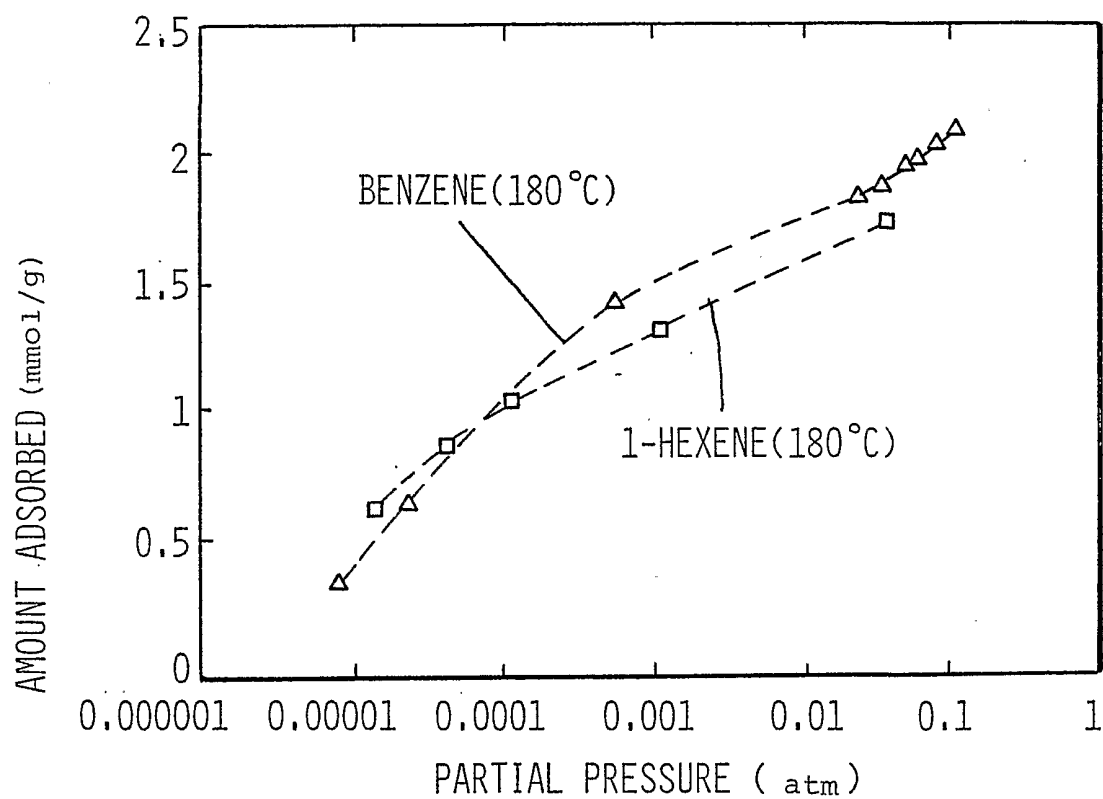


FIG-15

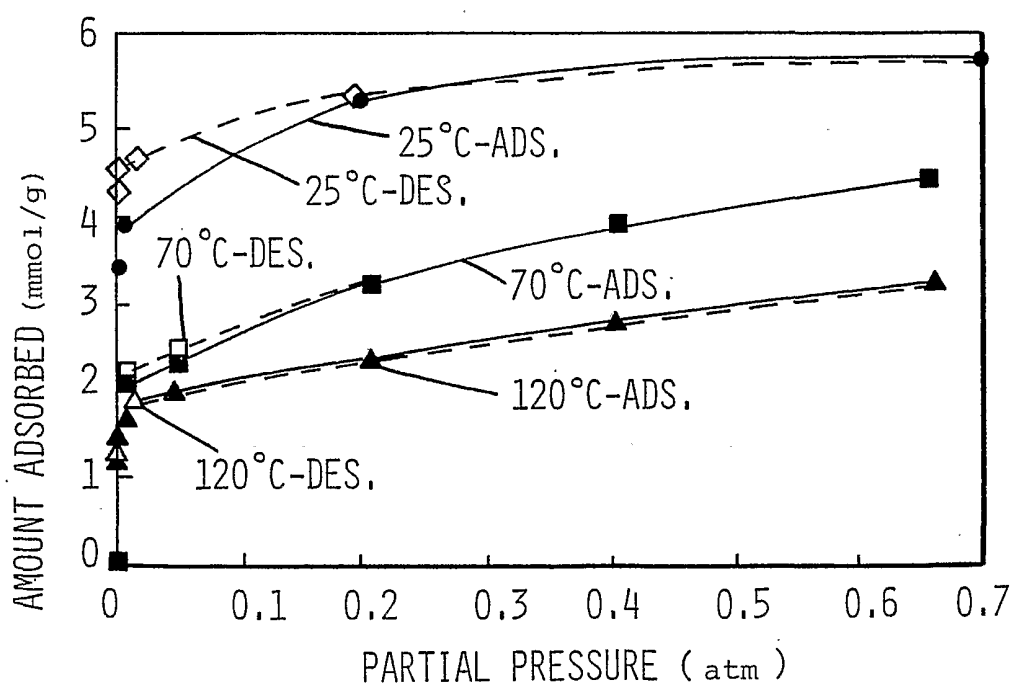


FIG-16

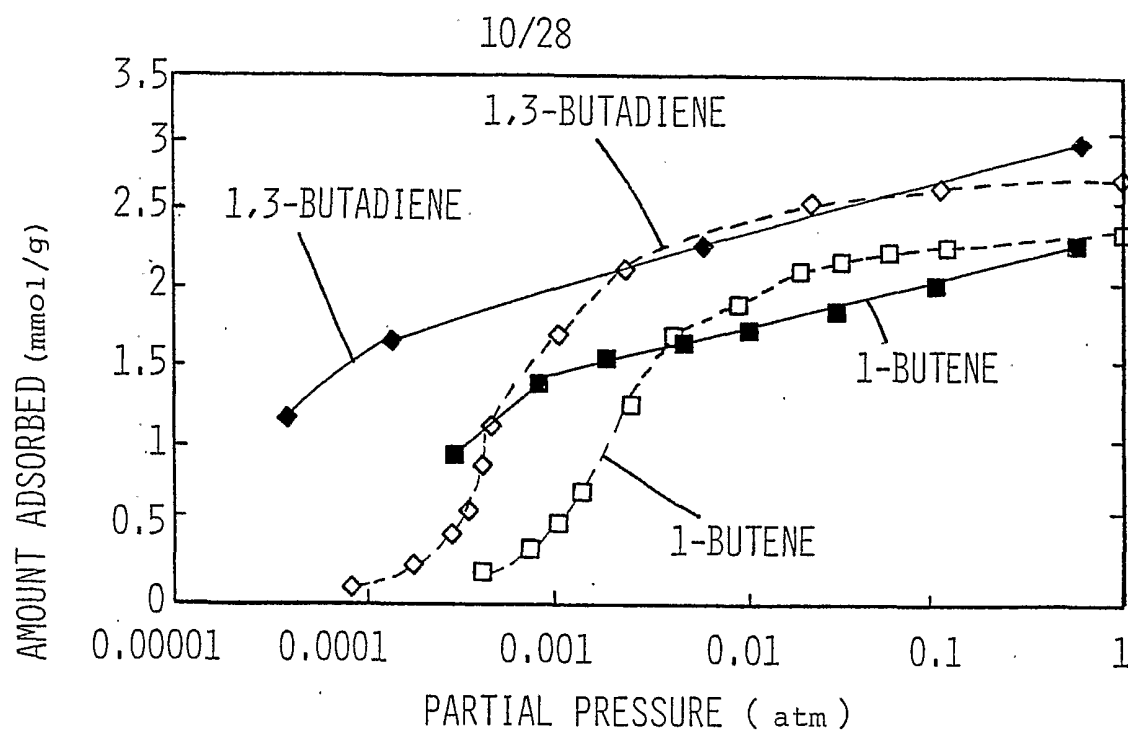


FIG-17

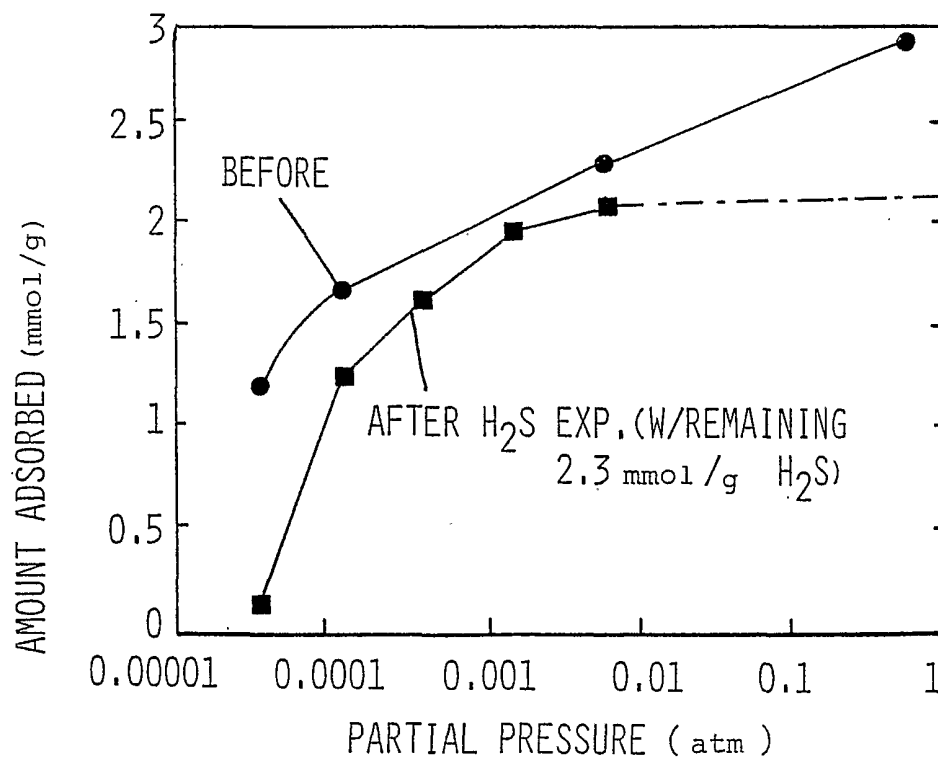


FIG-18

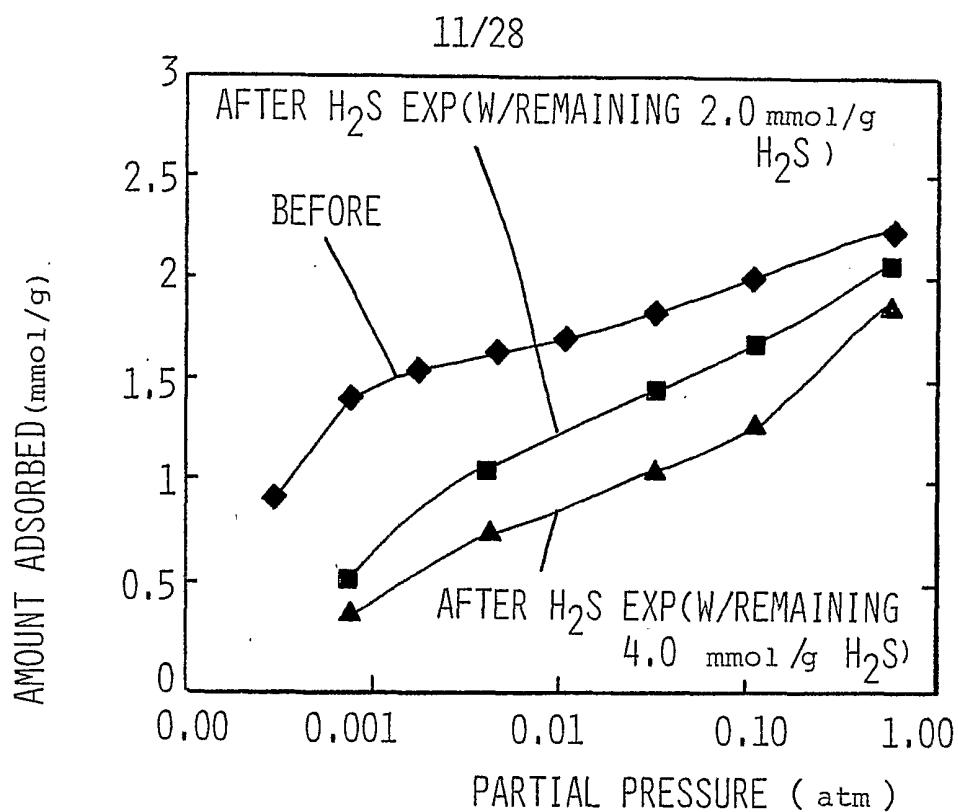


FIG-19

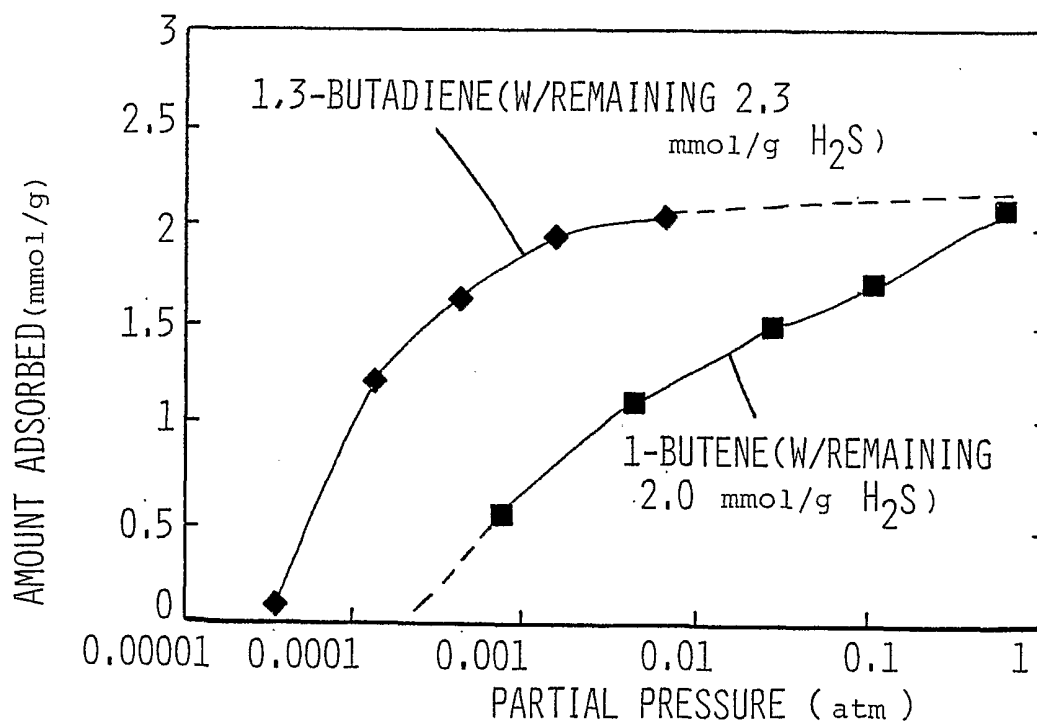


FIG-20

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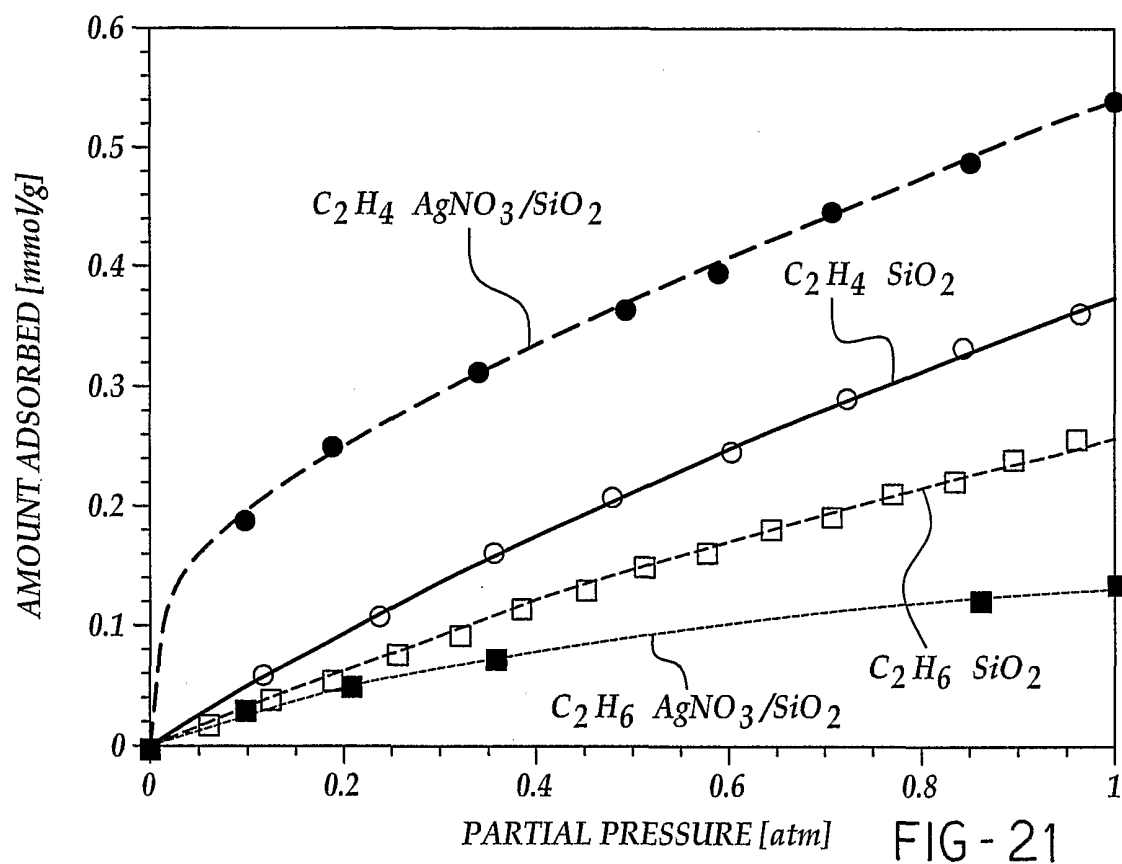


FIG - 21

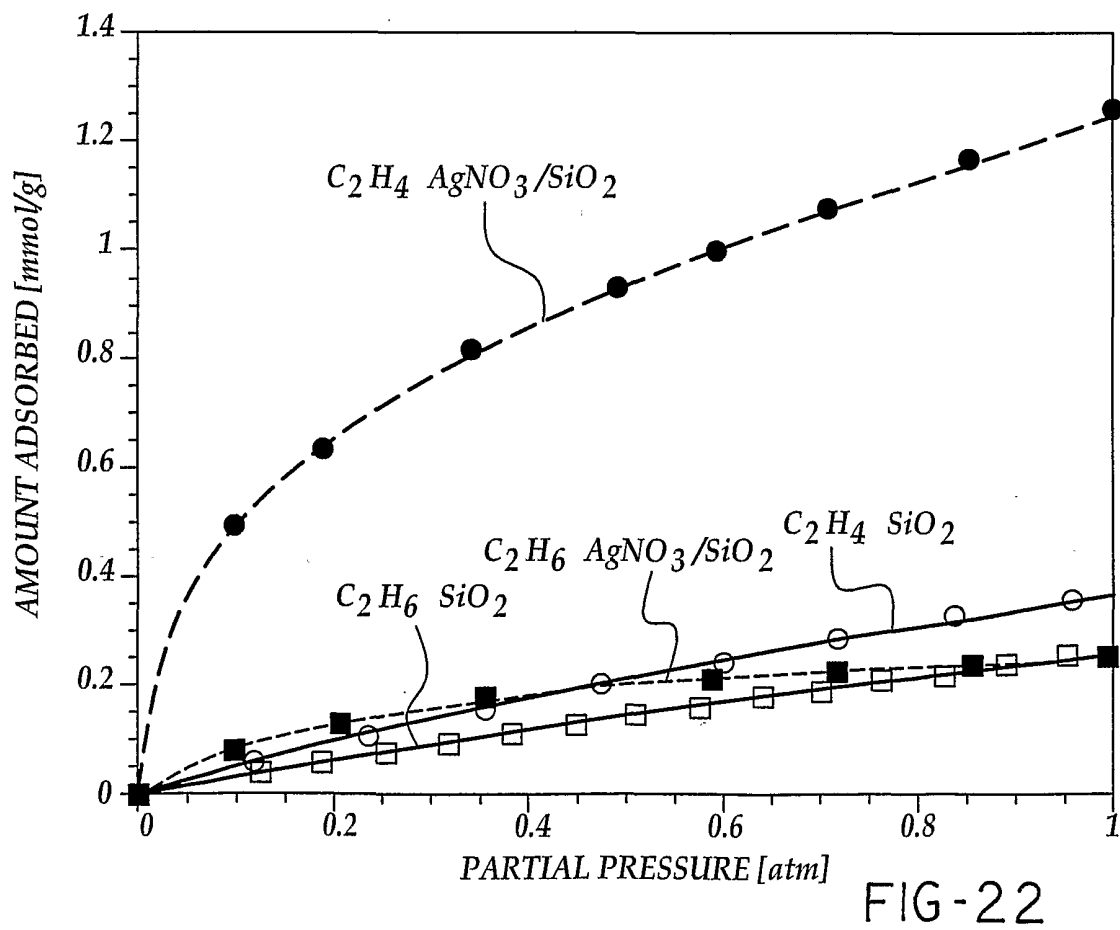


FIG - 22

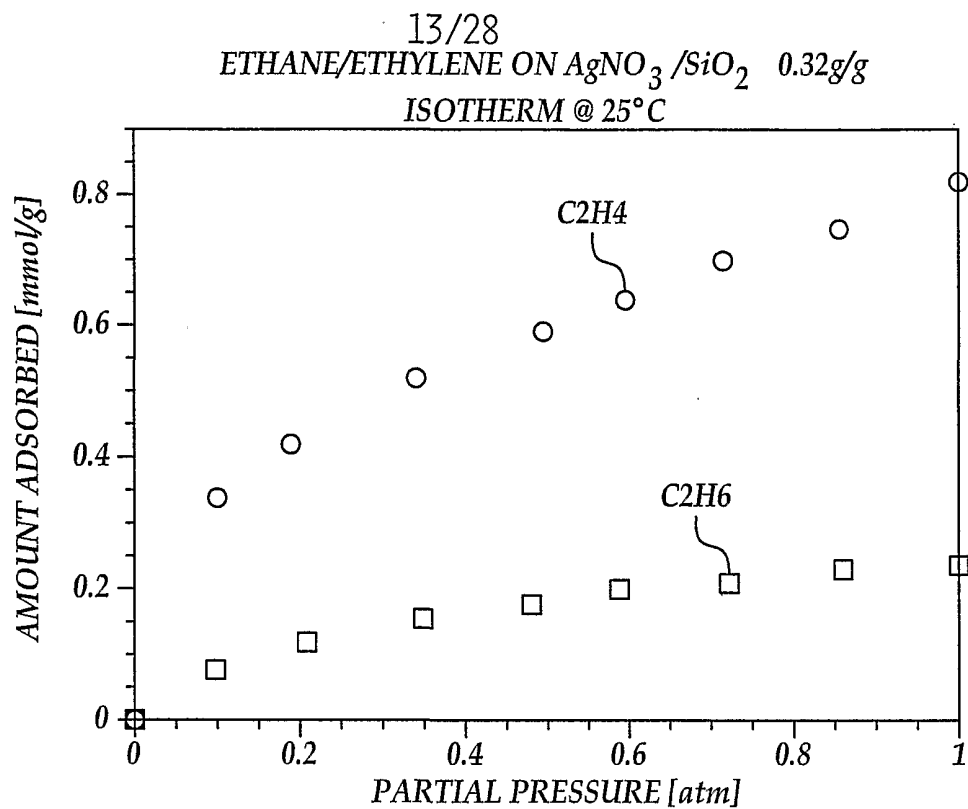


FIG-22A

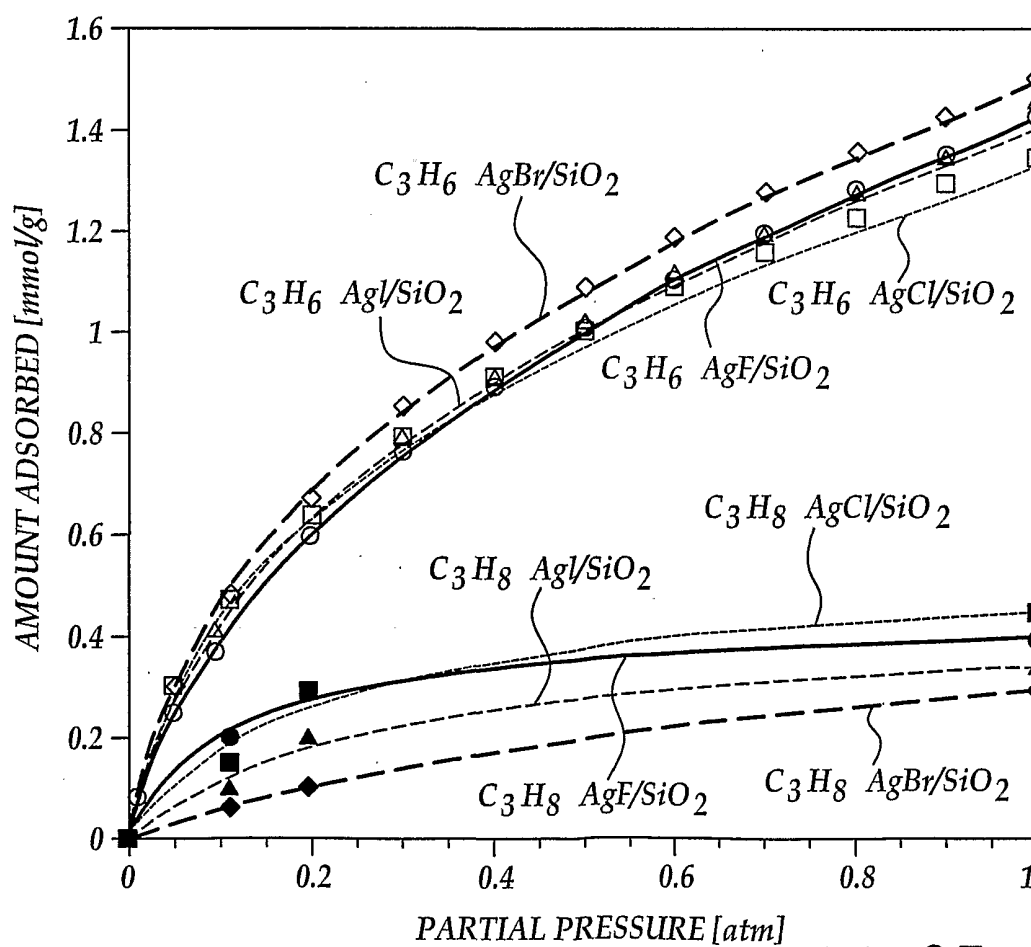


FIG-23

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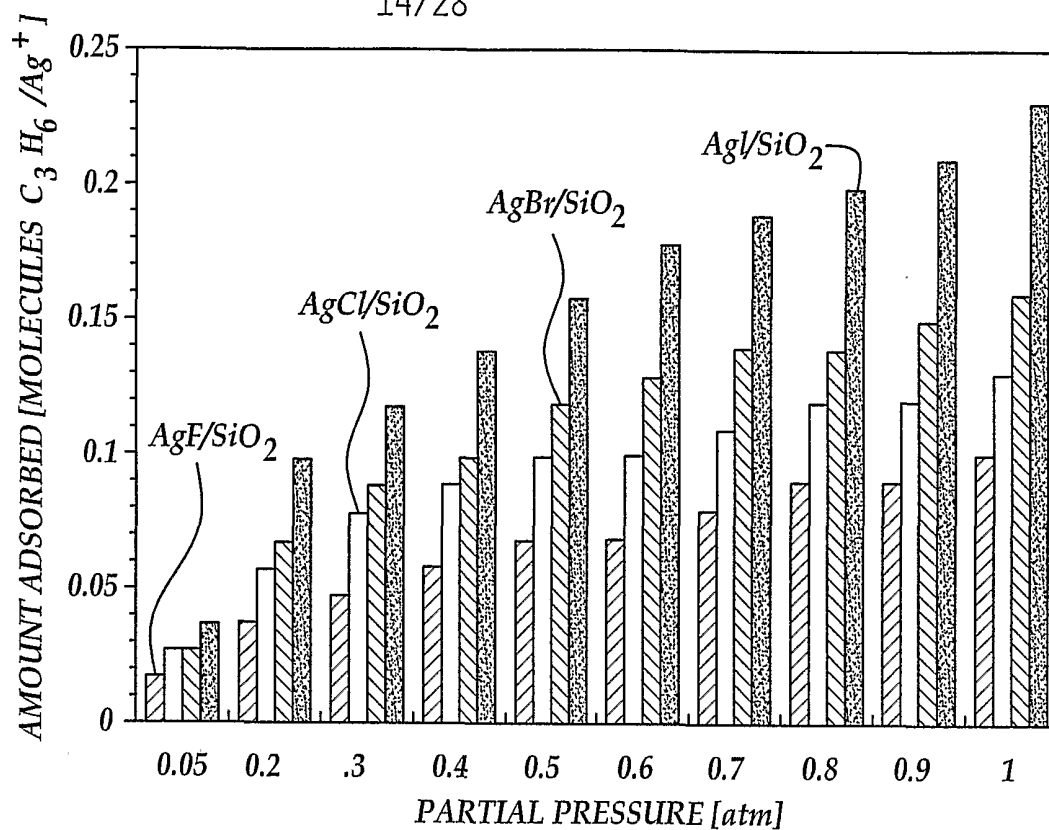


FIG - 24

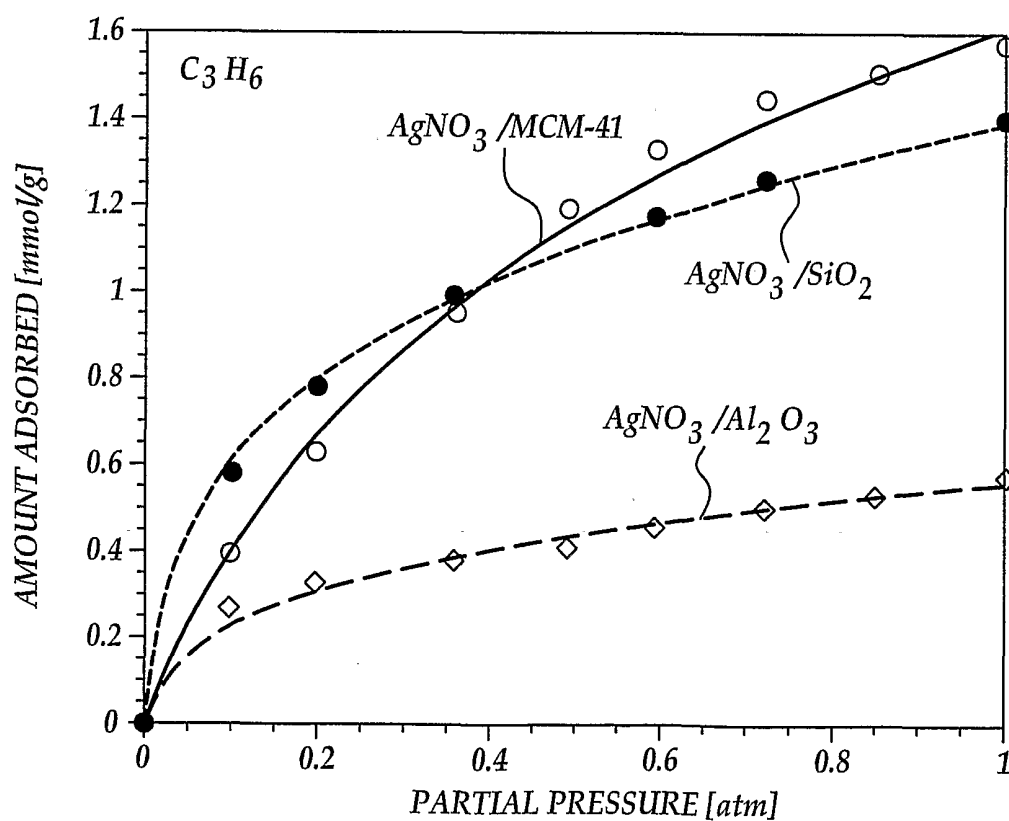


FIG - 25

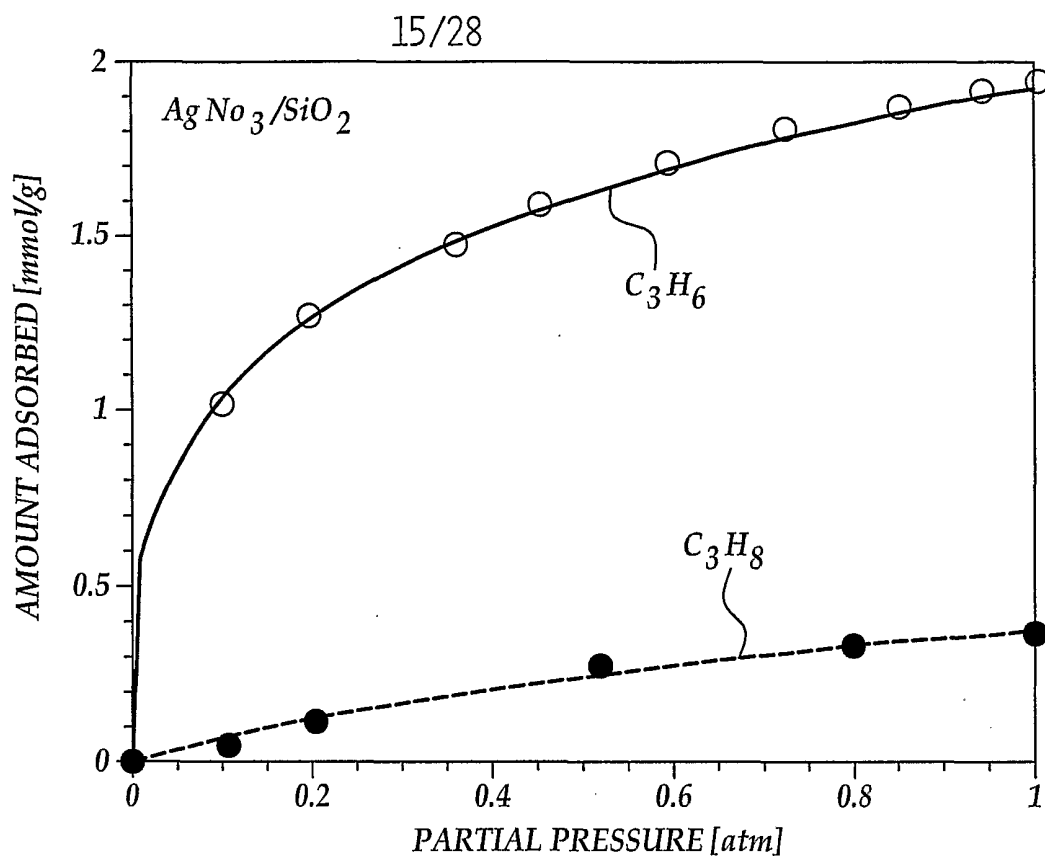


FIG - 26

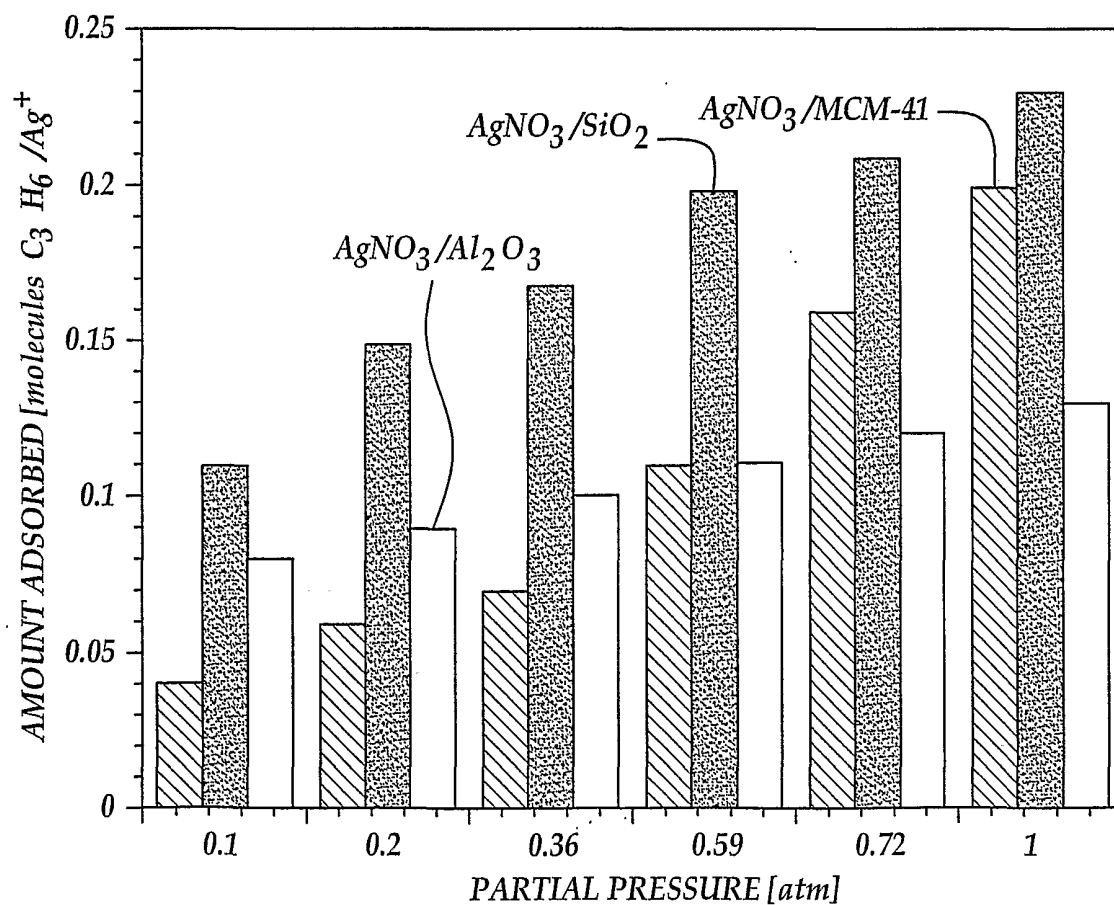


FIG - 27

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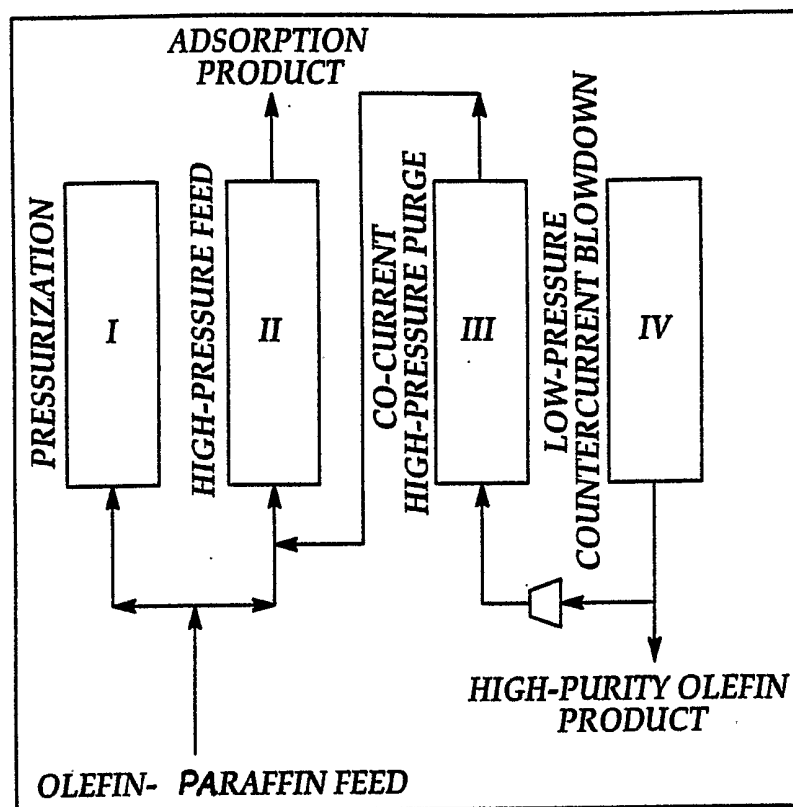


FIG-28

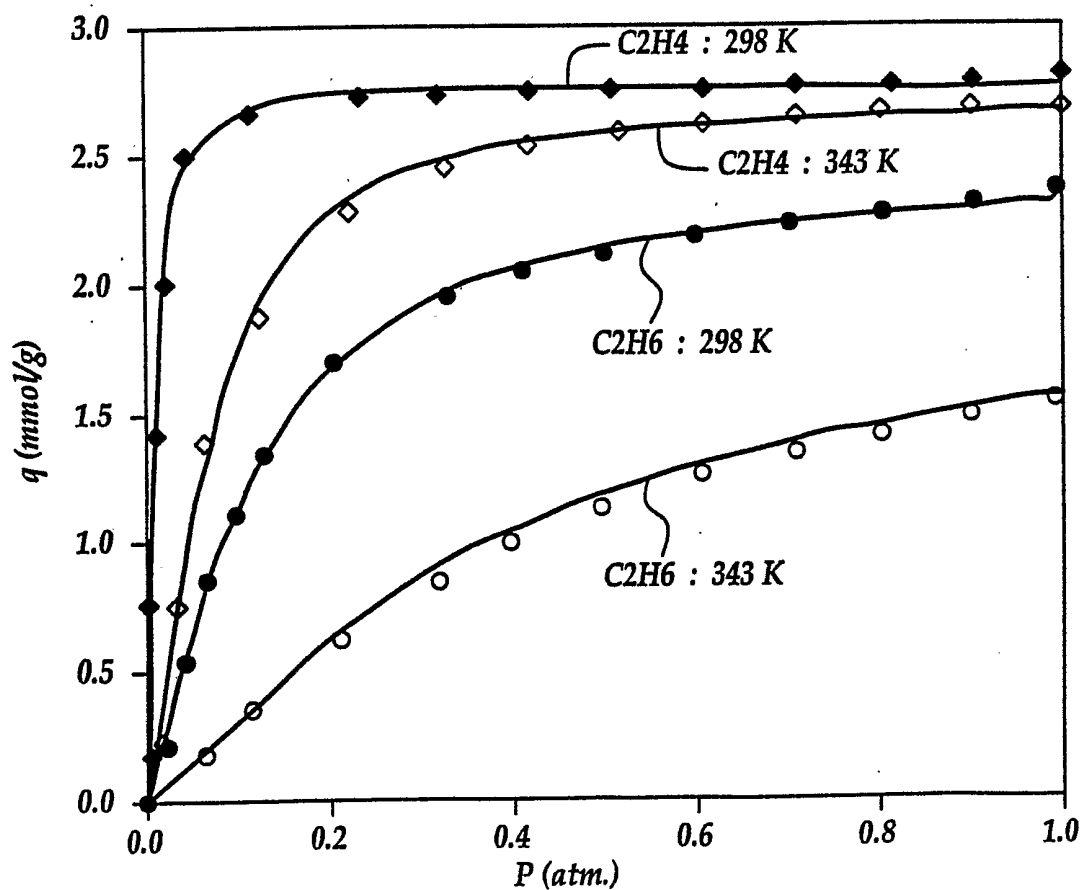


FIG-29

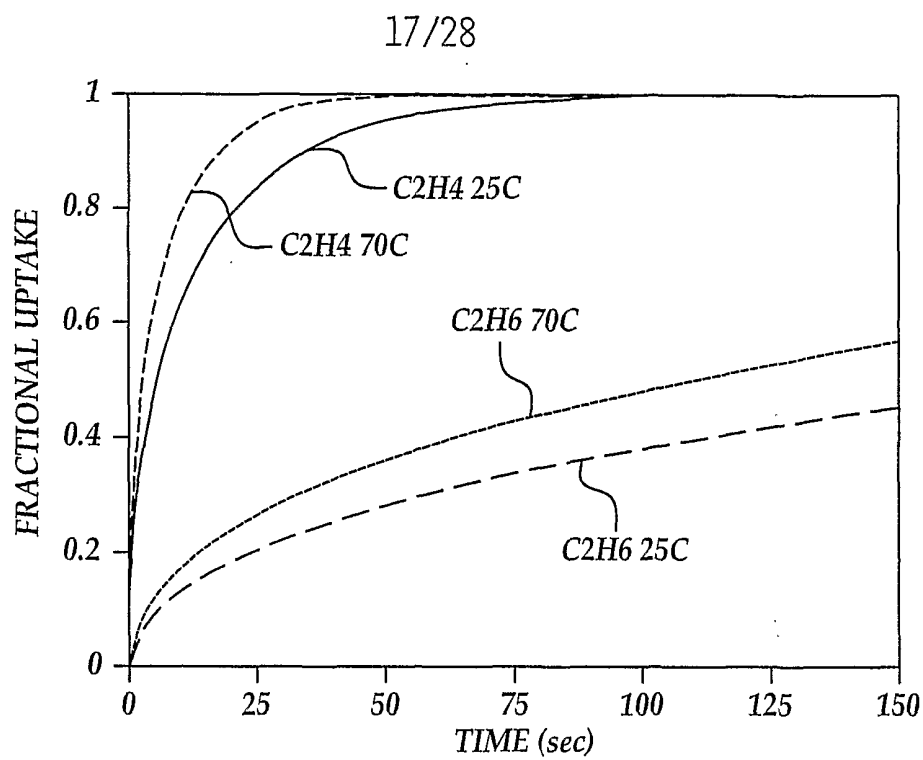


FIG-30

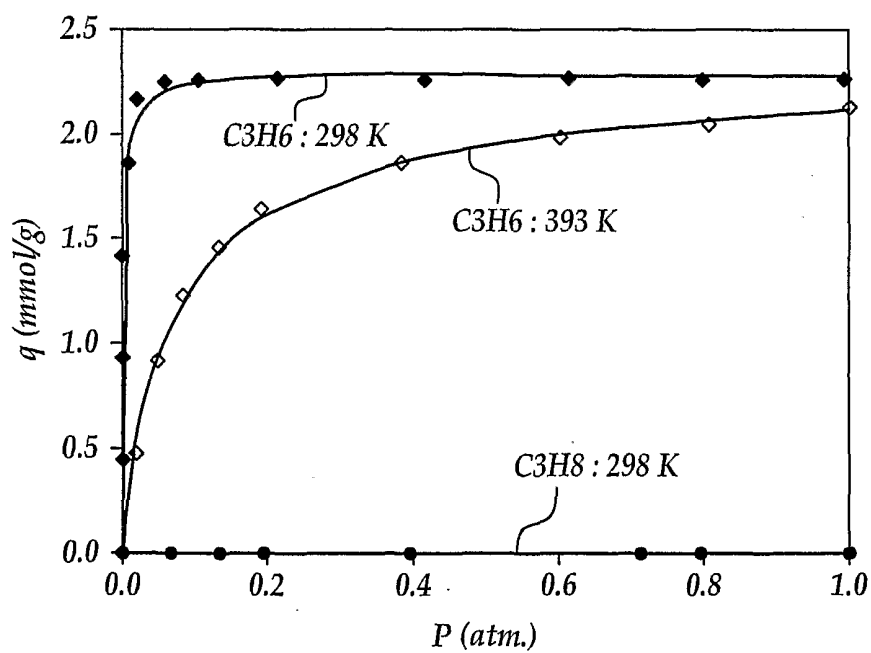


FIG-31

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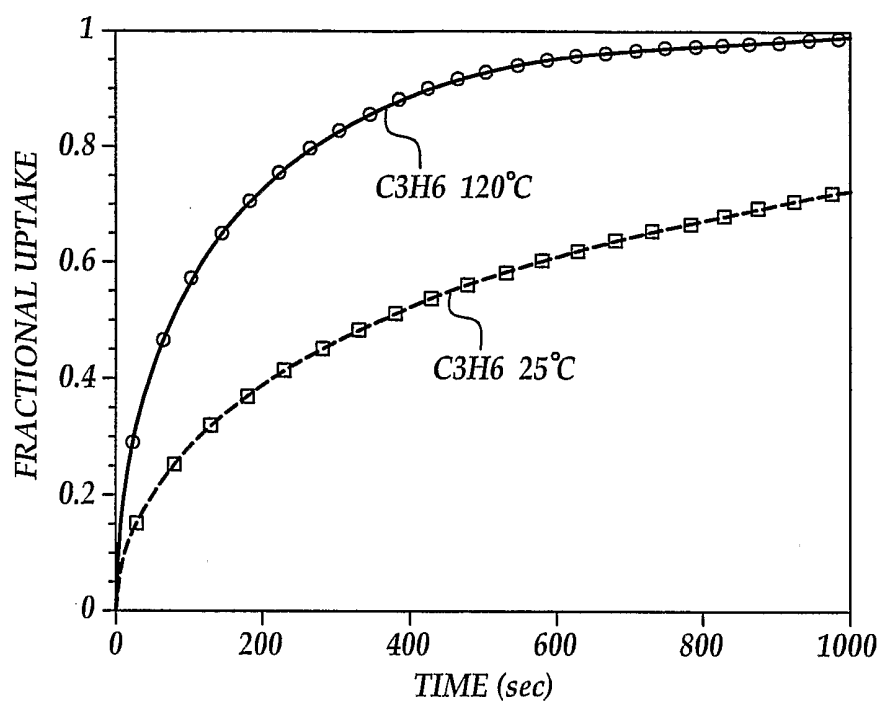


FIG - 32

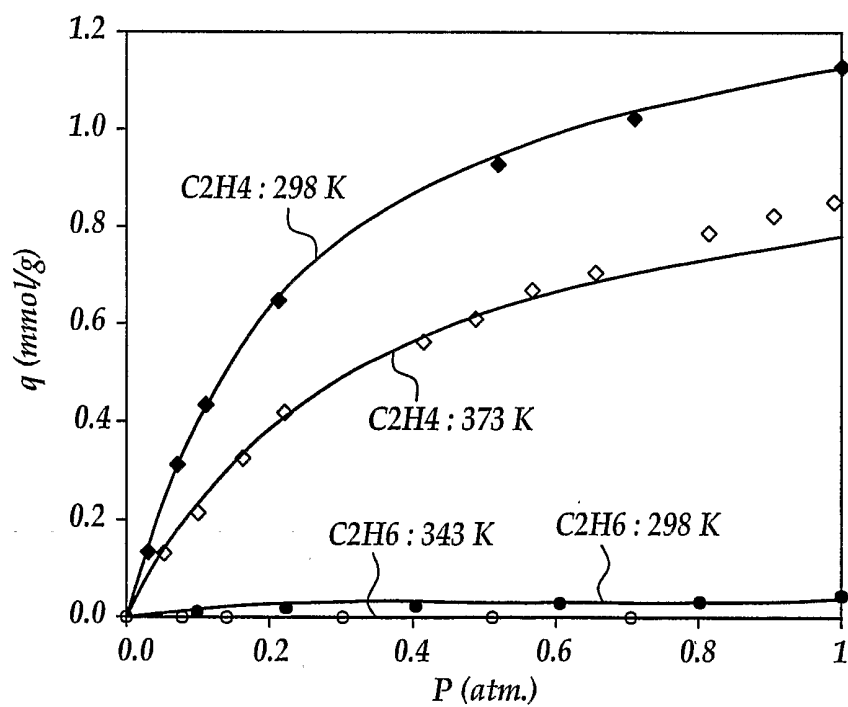


FIG - 33

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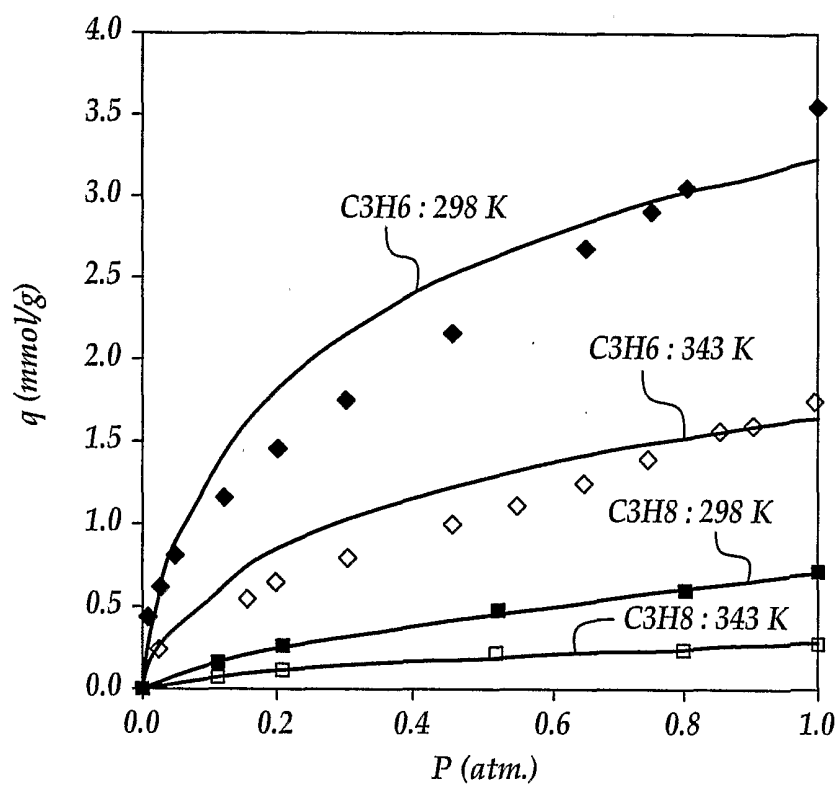


FIG- 34

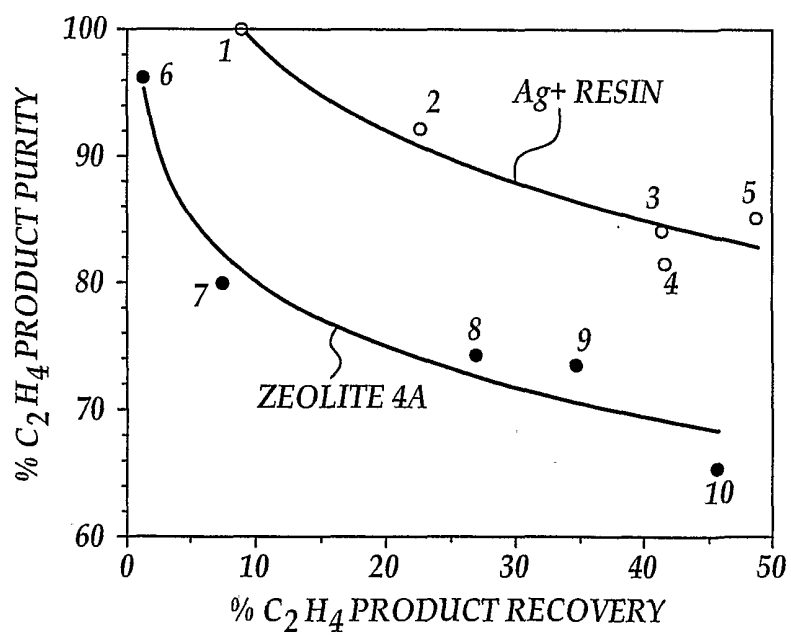


FIG- 35

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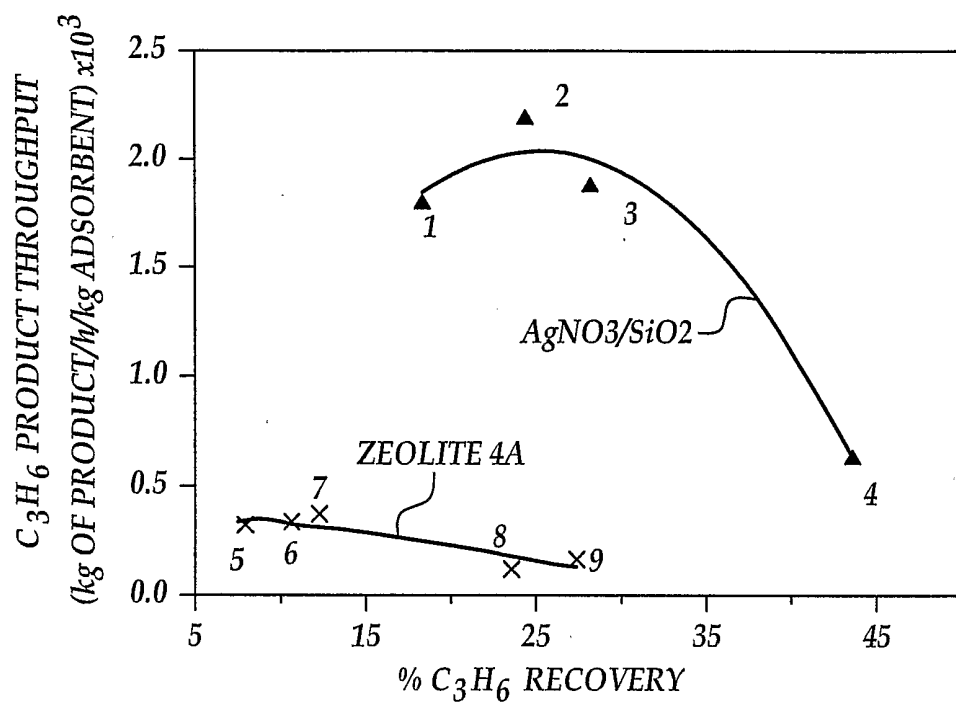


FIG - 36

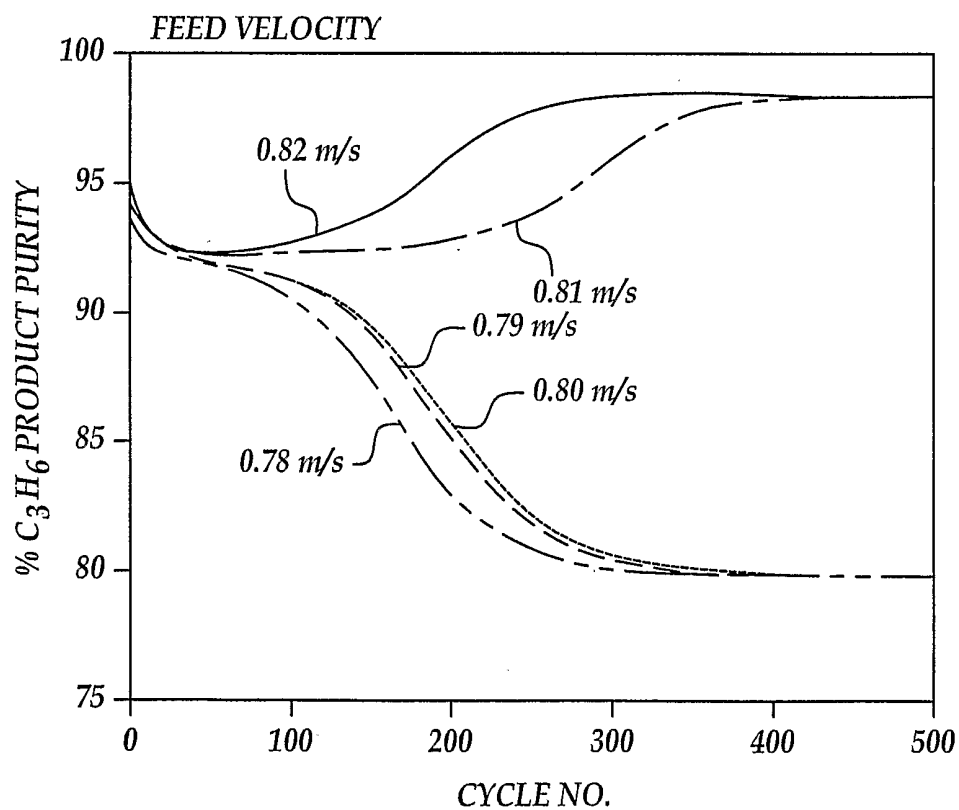


FIG - 37

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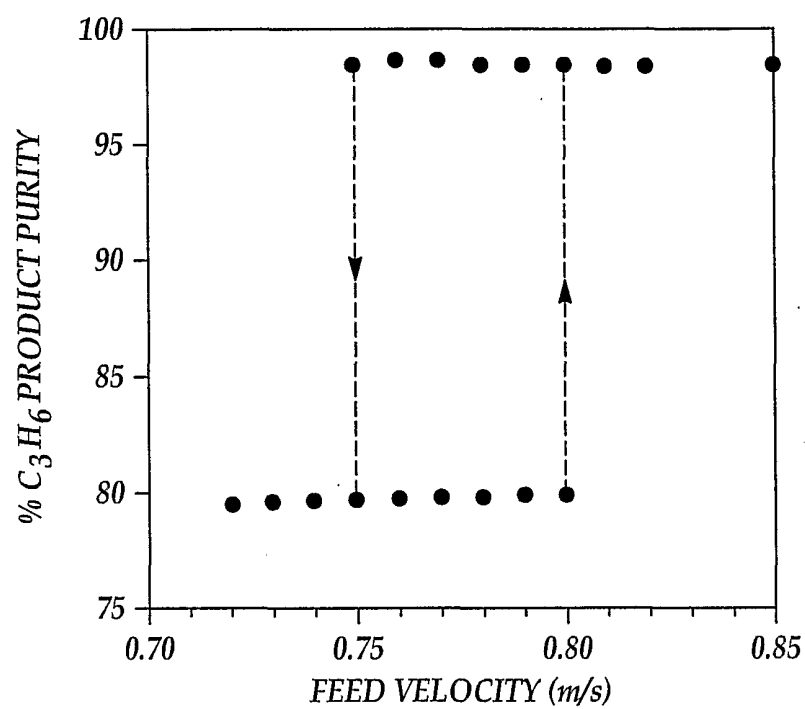


FIG - 38

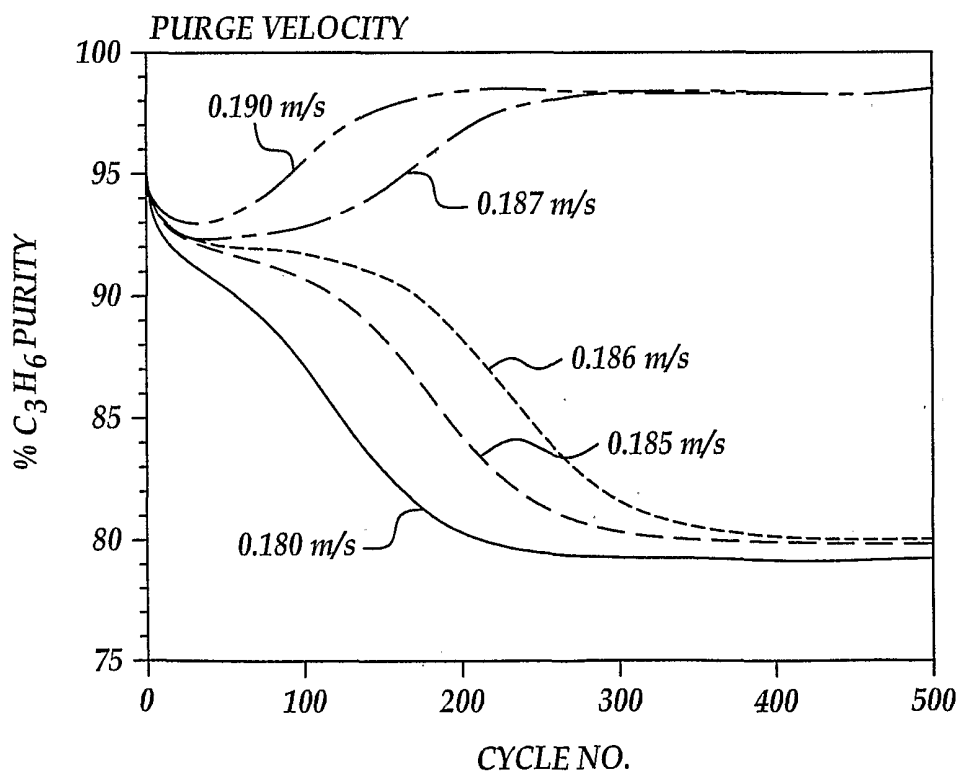


FIG - 39

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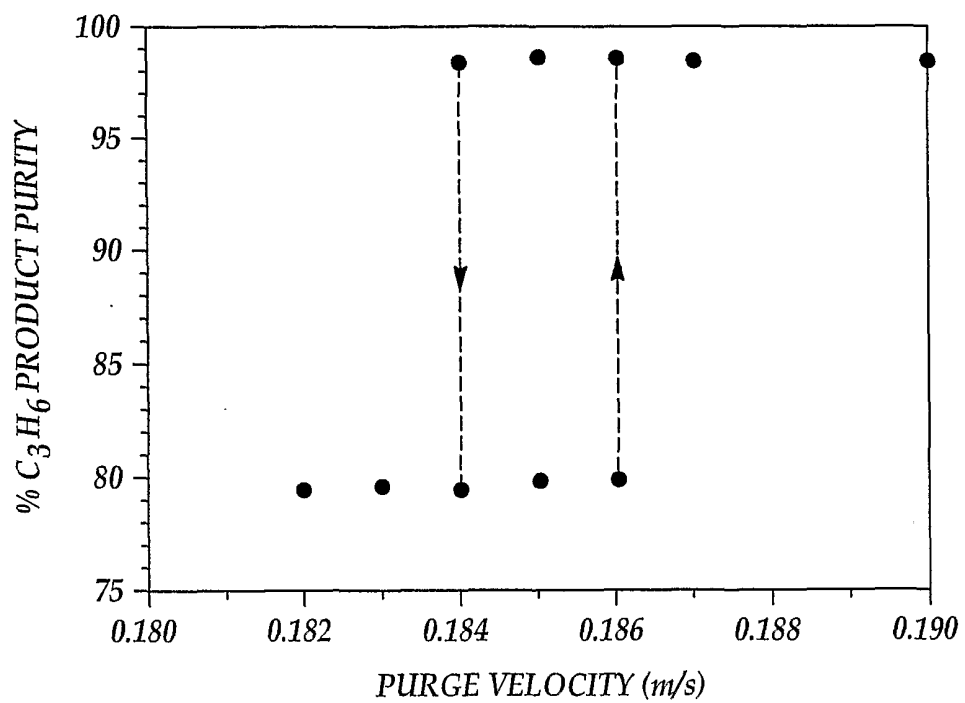


FIG- 40

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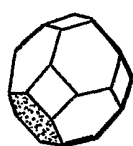


FIG-41A

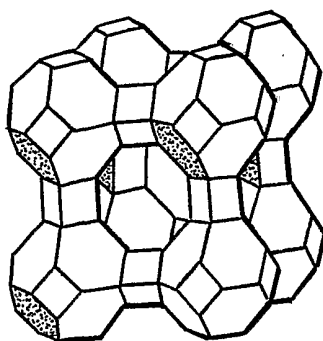


FIG-41B

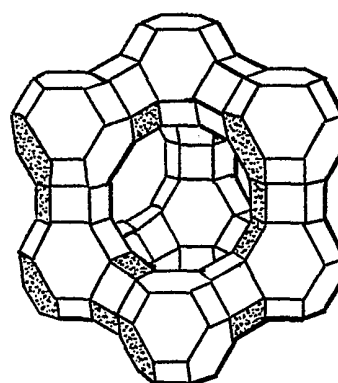


FIG-41C

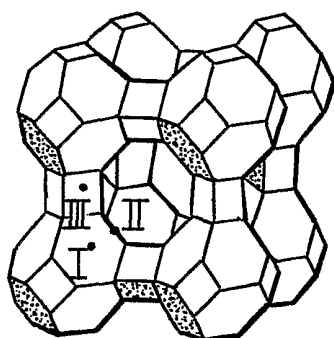


FIG-41D

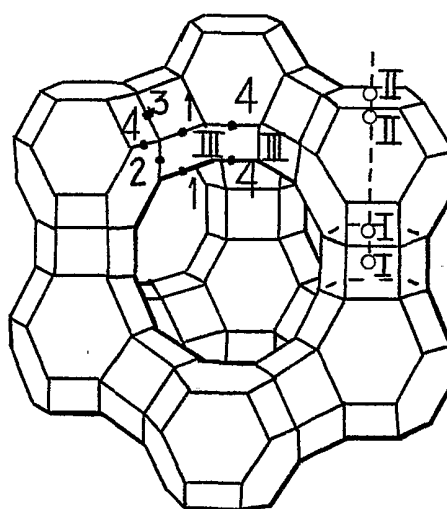


FIG-41E

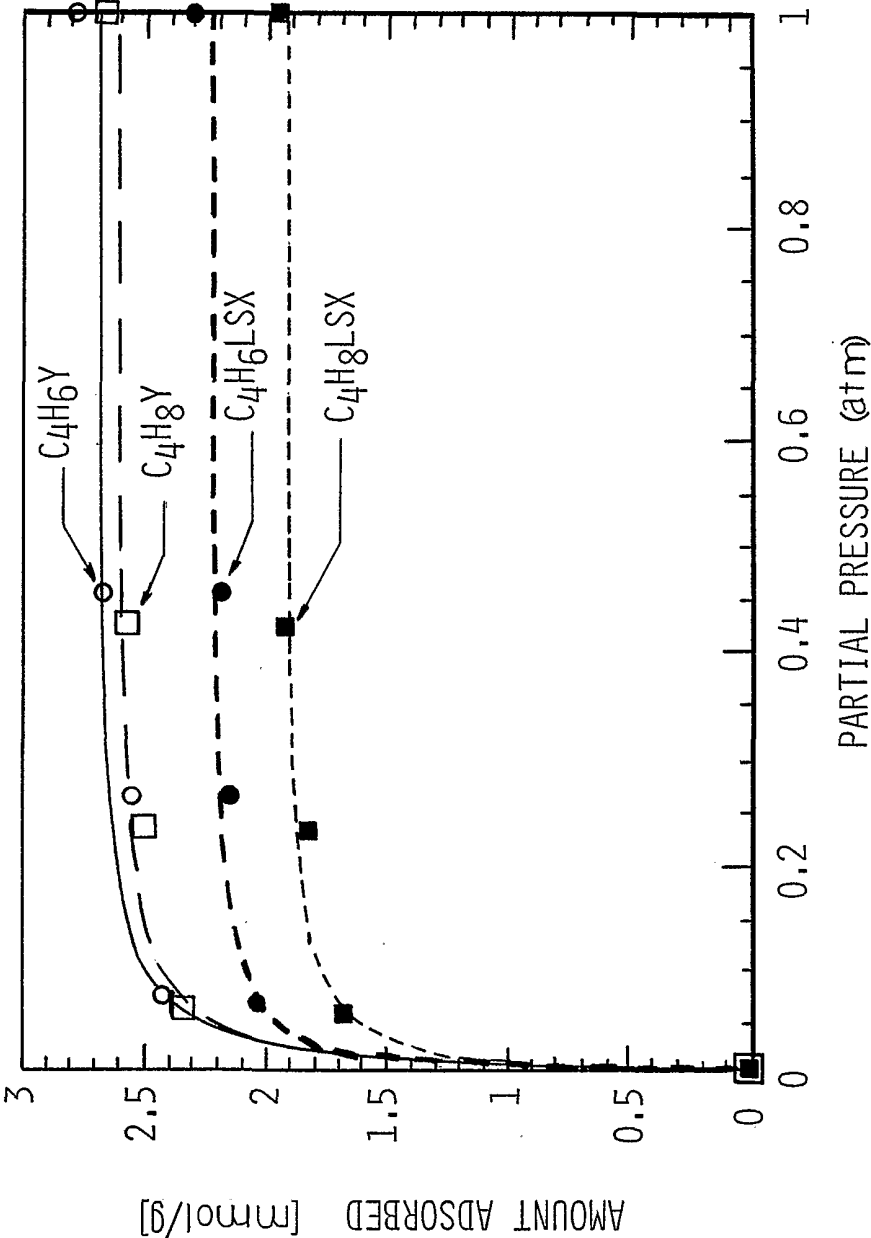


FIG-42

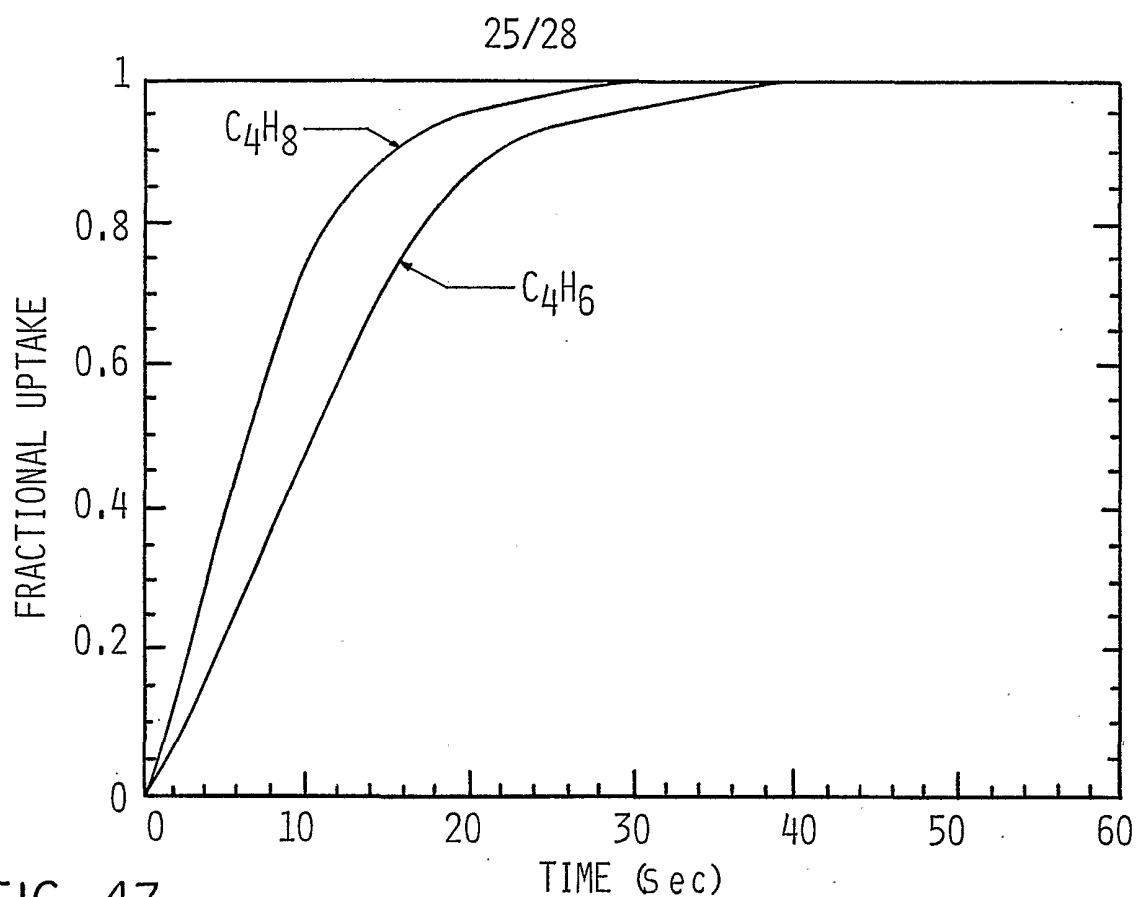


FIG - 43

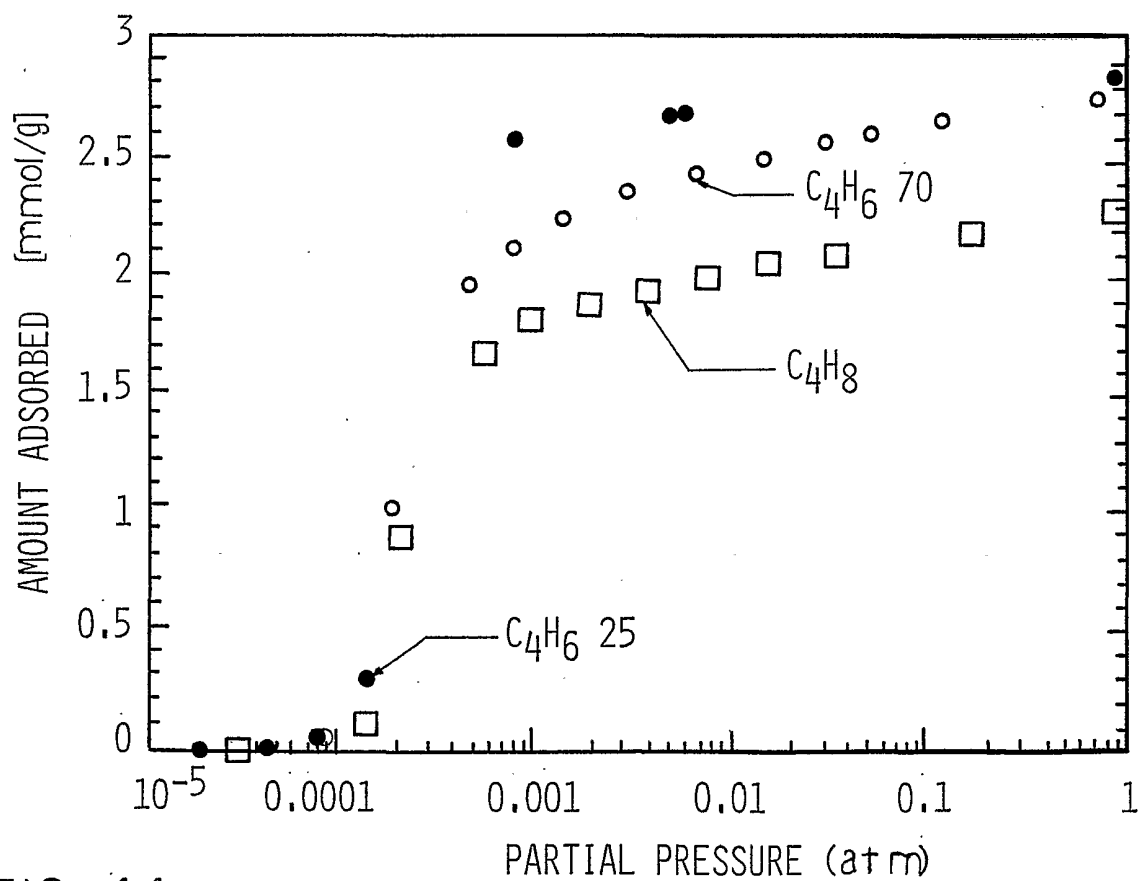


FIG - 44

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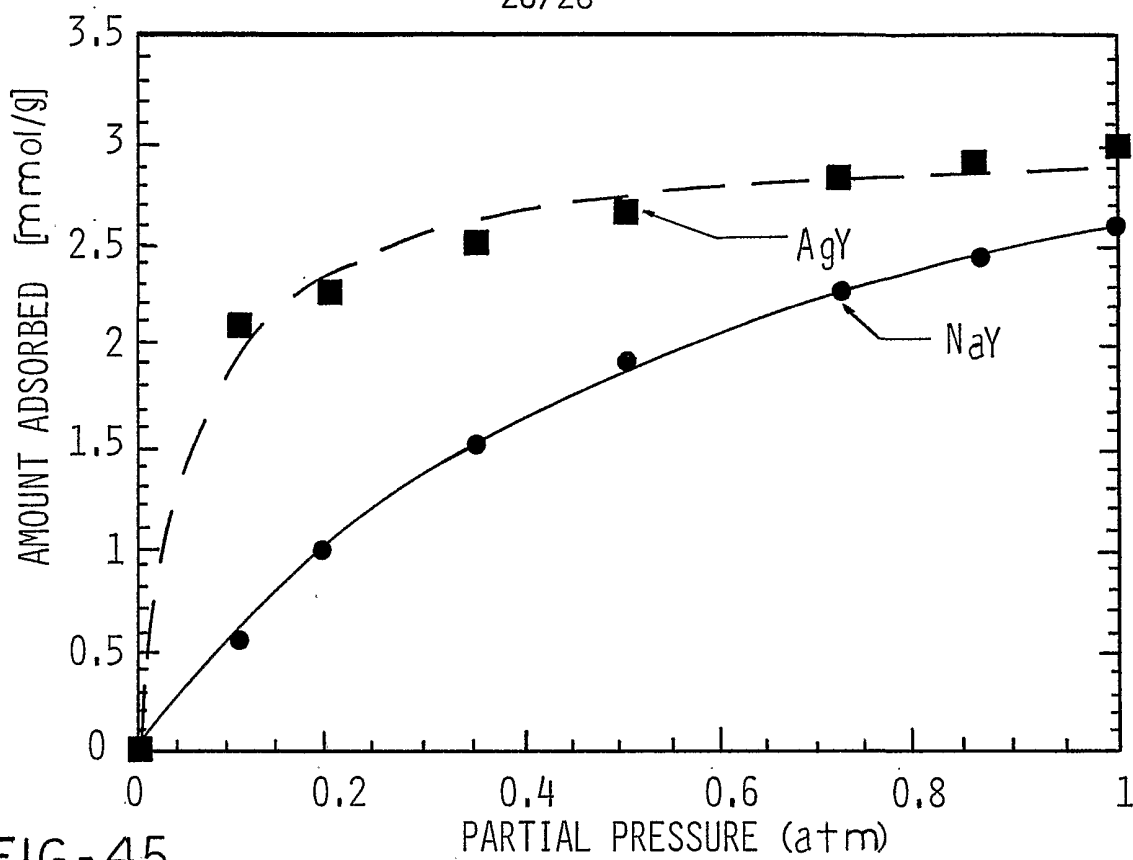


FIG-45

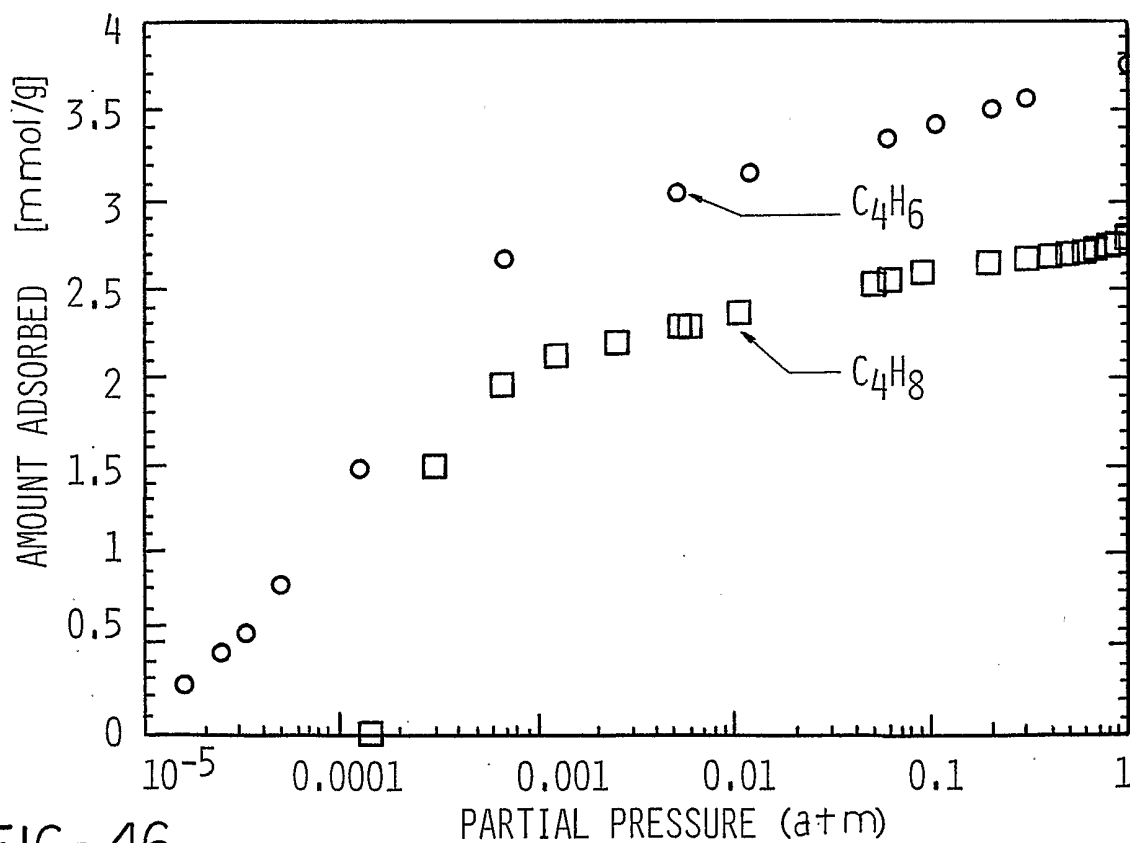
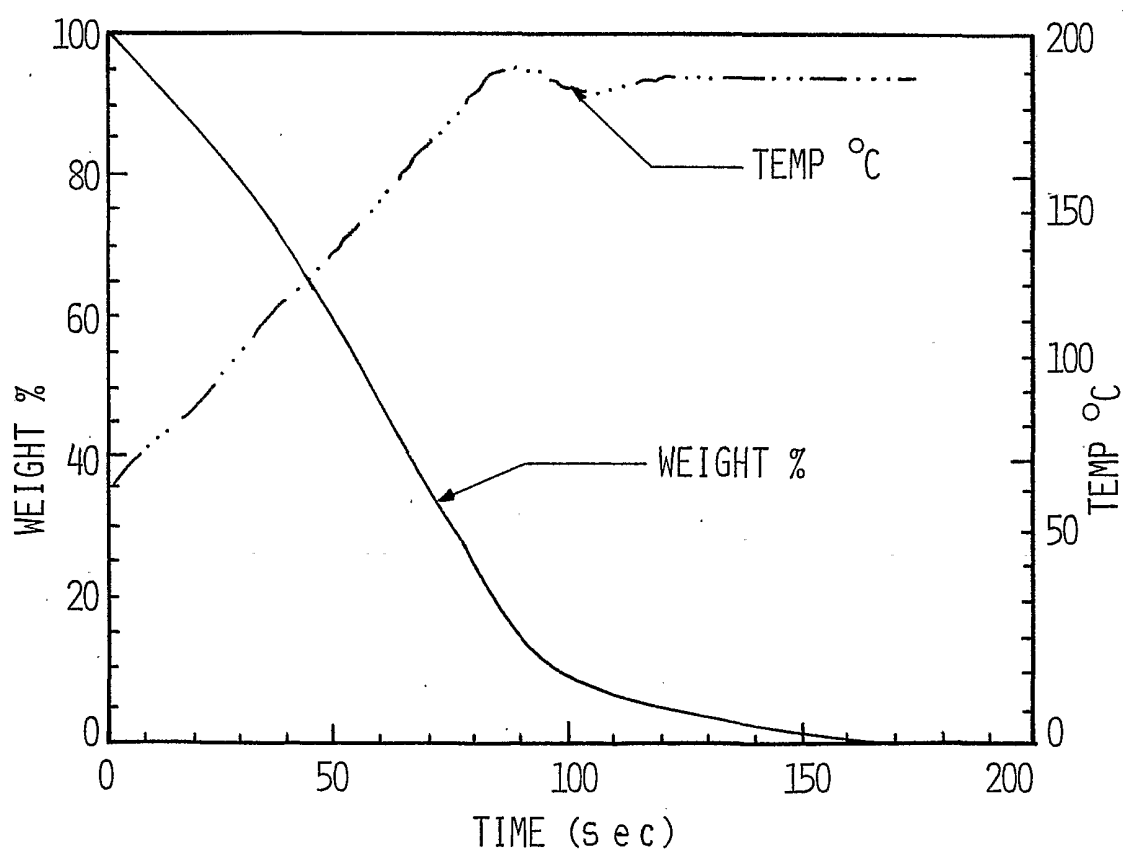
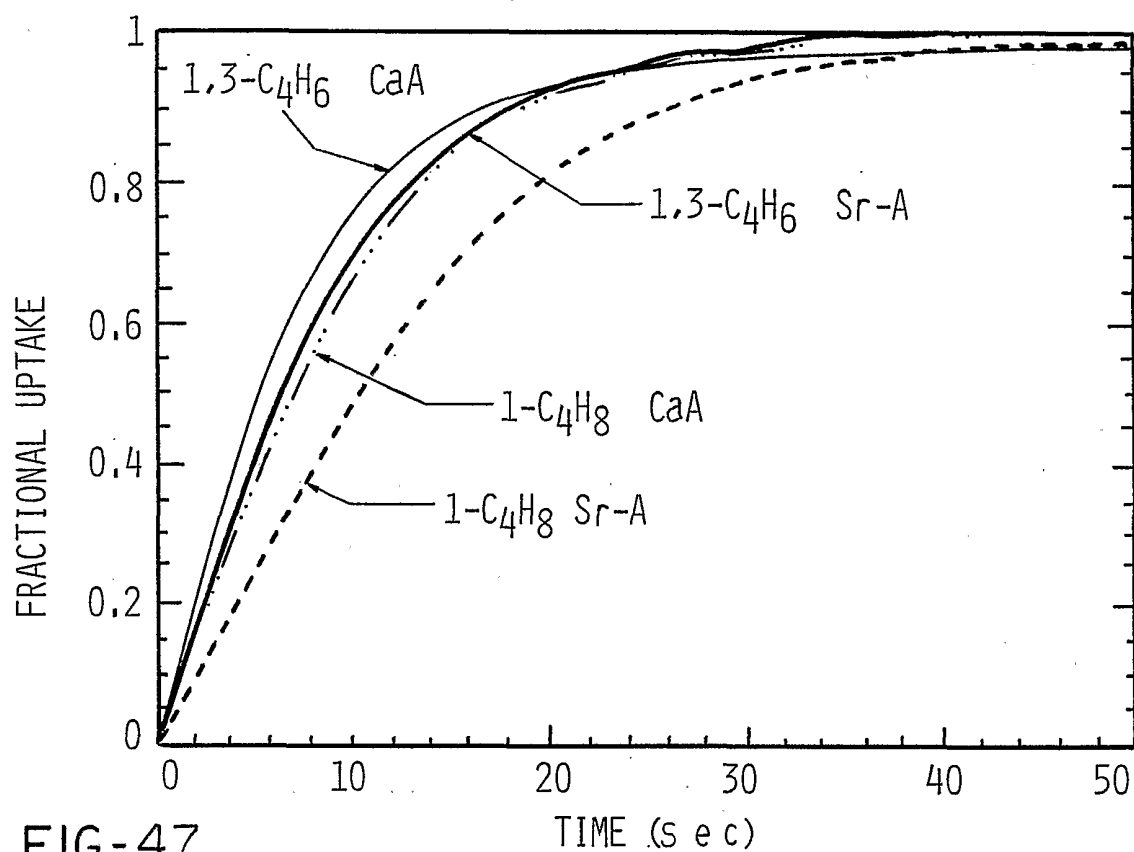


FIG-46

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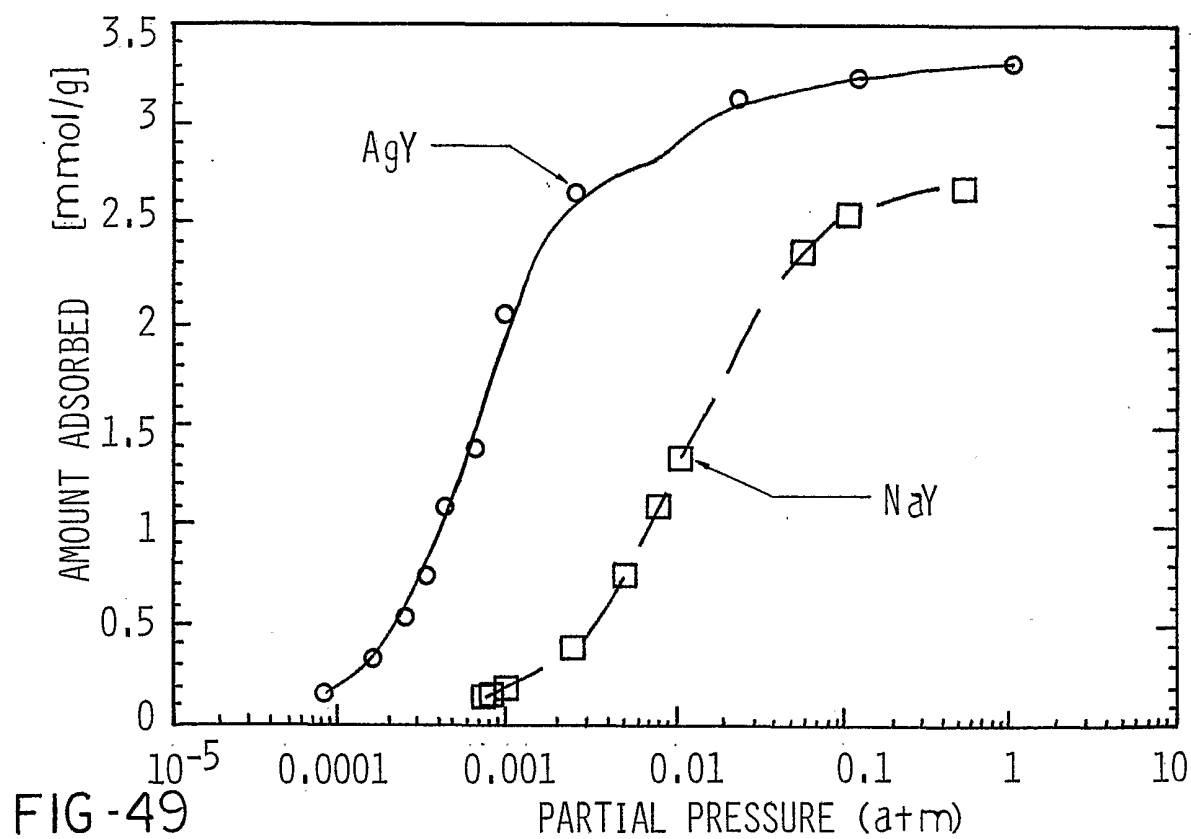


FIG-49

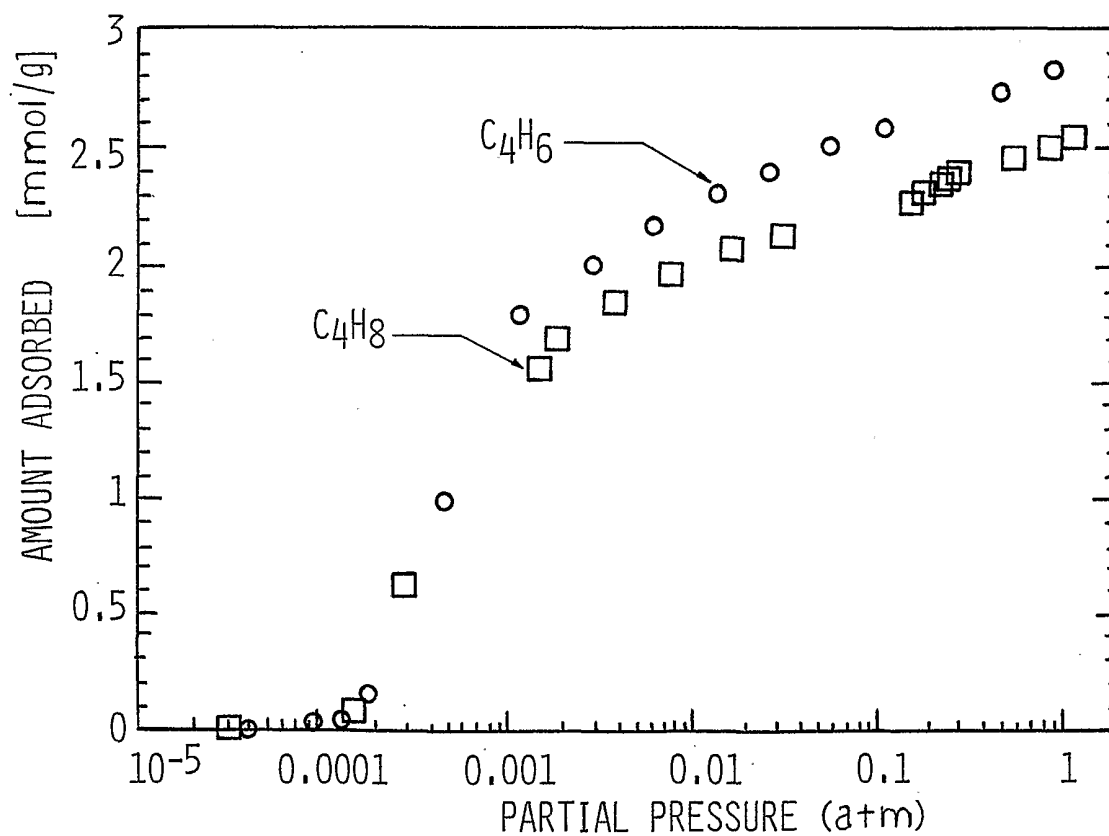


FIG-50

INTERNATIONAL SEARCH REPORT

International Application No
PC1/US 01/23190

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C/152 C07C/156 B01J20/02 C07C/13

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C C10G B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 354 316 A (HÜLS CHEMISCHE WERKE AG) 14 February 1990 (1990-02-14) claims; examples ---	16-26, 32
X	US 3 211 644 A (CLARK EDWARD L) 12 October 1965 (1965-10-12) column 5, line 37 - line 54 ---	27-29, 33
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A	WO 00 24695 A (THE REGENTS OF THE UNIVERSITY OF MICHIGAN; CHEVRON USA) 4 May 2000 (2000-05-04) claims --- -/--	16-29, 32, 33

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

17 January 2002

Date of mailing of the international search report

28. 01 2002

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Authorized officer

Van Geyt, J

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/23190

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2 606 938 A (ROBINSON SAM P) 12 August 1952 (1952-08-12) ---	
A	US 3 189 658 A (QUINN HAROLD W) 15 June 1965 (1965-06-15) ---	
A	US 3 243 471 A (STERN ERIC W) 29 March 1966 (1966-03-29) ---	
A	US 3 409 692 A (LONG ROBERT B ET AL) 5 November 1968 (1968-11-05) -----	

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 01/23190

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-15,30,31

Adsorbent comprising a carrier on which a silver or copper compound is deposited and its use for separating hydrocarbons having at least one double carbon-to-carbon bond from mixtures comprising also a sulphur compound

2. Claims: 16-26,32

process for separating a diene from a mixture comprising also a sulphur compound using zeolite X, zeolite Y or zeolite LSX, at least partially exchanged with silver or copper cations as adsorbent

3. Claims: 27-29,33

Process for separating a diene from a mixture comprising also a sulphur compound using zeolite A as adsorbent

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/23190

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