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(54) **CATALYSEURS HYBRIDES, COMPRENANT UNE ZEOLITE MICROPOREUSE ET UN COCATALYSEUR MESOPOREUX, POUR LA CONVERSION D'HYDROCARBURES ET D'AUTRES COMPOSES ORGANIQUES**

(54) **HYBRID CATALYSTS CONTAINING A MICROPOROUS ZEOLITE AND A MESOPOROUS COCATALYST, FOR THE CONVERSION OF HYDROCARBONS OR OTHER ORGANIC COMPOUNDS**

(57) Divulgation d'un nouveau catalyseur hybride utile pour la conversion d'hydrocarbures et d'autres composés organiques. Ce catalyseur comprend de 70 à 85 %, en poids, de particules microporeuses de type zéolite noyées dans de 10 à 30 %, en poids, de particules solides mésoporeuses plus grosses, ces dernières servant de cocatalyseur. Facultativement, on peut utiliser jusqu'à 20 %, en poids, d'un liant argileux inerte. De préférence, les particules de type zéolite sont des particules de structure ZSM-5 et se trouvent sous forme acide. De préférence également, les particules solides mésoporeuses utilisées comme cocatalyseur sont des particules d'un oxyde choisi parmi le groupe constitué de la silice, de l'alumine, du silicate d'alumine, des oxydes de magnésium, de titane, de fer, de zirconium, de chrome et de nickel, et de mélanges de ces composés. De préférence, l'oxyde mésoporeux agit également comme support pour une espèce déshydrogénante choisie parmi le groupe constitué des oxydes de gallium, de zinc, de manganèse, de chrome et de molybdène, des métaux précieux, des oxydes de métaux précieux et des mélanges de ces composés.

(57) There is provided a novel hybrid catalyst suitable for the conversion of hydrocarbons and other organic compounds. The catalyst comprises 70 wt % to 85 wt % of microporous zeolite-type particles embedded in 10 wt % to 30 wt % of larger mesoporous solid particles, the latter being used as a cocatalyst. Optionally, up to about 20 wt% of an inert clay binder may be used. Preferably, the zeolite-type particles are particles having the ZSM-5 structure and in the acidic form. Also preferably, the mesoporous solid particles used as a cocatalyst are particles of an oxide selected from the group consisting of silica, alumina, aluminosilica, magnesium oxide, titanium oxide, iron oxide, zirconium oxide, chromium oxide, nickel oxide, and mixtures thereof. Also preferably, the mesoporous oxide acts as a support for a dehydrogenating species selected from a group consisting of gallium oxide, zinc oxide, manganese oxide, chromium oxide, molydennum oxide, tungsten oxide, a precious metal, a precious metal oxide, and mixtures thereof.

ABSTRACT

There is provided a novel hybrid catalyst suitable for the conversion of hydrocarbons and other organic compounds. The catalyst comprises 70 wt % to 85 wt % of microporous zeolite-type particles embedded in 10 wt % to 30 wt % of larger mesoporous solid particles, the latter being used as a cocatalyst. Optionally, up to about 20 wt% of an inert clay binder may be used. Preferably, the zeolite-type particles are particles having the ZSM-5 structure and in the acidic form. Also preferably, the mesoporous solid particles used as a cocatalyst are particles of an oxide selected from the group consisting of silica, alumina, aluminosilica, magnesium oxide, titanium oxide, iron oxide, zirconium oxide, chromium oxide, nickel oxide, and mixtures thereof. Also preferably, the mesoporous oxide acts as a support for a dehydrogenating species selected from a group consisting of gallium oxide, zinc oxide, manganese oxide, chromium oxide, molydennum oxide, tungsten oxide, a precious metal, a precious metal oxide, and mixtures thereof.

TITLE OF THE INVENTION:

Hybrid catalysts containing a microporous zeolite and a mesoporous cocatalyst, for the conversion of hydrocarbons or other organic compounds

BACKGROUND OF THE INVENTION

1. Field of Invention

The present invention relates to the field of catalysts for the conversion of hydrocarbons and other organic compounds.

2. The Prior Art

Catalysts are widely used in the petrochemical industry for the production of a large variety of commodity chemicals such as BTX (benzene, toluene, xylenes) aromatics as well as reformates.

For the conversion of hydrocarbons or other organic compounds, it is known to use multifunctional catalysts. Multifunctional means that one catalyst is apt to perform at least two distinct catalytic functions. Bifunctional catalysts is a term used to refer to catalysts capable of performing two main functions. Most multifunctional catalysts are hybrid in the sense that they combine more than one substance on a solid support.

In the case of bifunctional catalysts, the main catalytic function is commonly performed by the catalyst's acid sites while metal species incorporated onto the same catalyst surface are often used to catalyze the chemical conversion of reaction intermediates generated at the acid sites. For example, metal species are often used for dehydrogenating/hydrogenating effects which may be important in several multi-step reactions. However, in some cases, the redox properties of these metal species are only used to keep the catalyst surface clean from the coke which is

otherwise formed in significant amounts over the acidic sites.

In classical bifunctional catalysis, the metal species are incorporated into locations which are sufficiently close to those of the acid sites in order to achieve efficient interactions with the reaction intermediates produced by these acid sites.

However, multifunctional catalysts of the prior art have merely provided for the mechanical mixture of two types of solid particles of catalysts generally support by a binder. Although such arrangements provide close contact between catalyst particles, external surfaces do not bind to each other to create conditions for strong synergistic interactions. This has in turn limiting effects on the product yields conferred by the use of those catalysts. Furthermore, the on-stream stability and activity of these catalysts is often problematic because of coke deposition on active site or other physical and chemical breakdowns.

Thus, despite advances in the art, there remains a need for improved multifunctional catalysts and for processes for making such catalysts. Ideally, multifunctional catalysts will perform several catalytic functions for the effective and selective conversion of hydrocarbons or other organic compounds.

It is therefore an object of the present invention to provide a novel and improved multifunctional catalysts and methods of making them. A related object is to provide a multifunctional catalysts with improved product yields and longer on-stream catalyst stability and activity over the catalysts of the prior art.

SUMMARY OF THE INVENTION

The present invention provides a novel and improved hybrid and multifunctional catalyst system. The hybrid catalysts of the present invention comprising two components: microporous particles embedded in mesoporous particles. Optionally,

a binder may be used to solidify the catalysts. The microporous component is a zeolite-type crystalline aluminosilicate or another similar material, which may be in the protonic form and/or have some active metallic or metal oxide species incorporated into the pore network. The mesoporous component may be a (reducible or irreducible) oxide, which preferably support some active metallic or metal oxide species.

Generally, the weight proportion of the zeolite component will vary from 70 to 85 wt%, that of the mesoporous component from 10 to 30 wt%, and that of the binder from 0 to 20 wt%.

The active metallic species which may be incorporated into the zeolite particles include Ga and Zn. The active metallic species which may be supported on the mesoporous component surface include Ga, Zn, Mn, Cr, Mo, W, or a metal or oxide of group VIII. Preferably, the microporous component exhibits acidic sites while the mesoporous component surface possesses dehydrogenating sites.

The present invention also relates to a method of making the novel and improved catalysts. The method comprises embedding the particles of the microporous material in the larger particles of the mesoporous material using the technique of extrusion and hot pressing with or without a binder.

Other objects and further scope of applicability of the present invention will become apparent from the detailed description given hereinafter. It should be understood, however, that this detailed description, while indicating preferred embodiments of the invention, is given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art.

DETAILED DESCRIPTION OF THE INVENTION

Before describing the present invention in detail, it is to be understood that the invention is not limited in its application to the details of construction and parts illustrated in the accompanying drawings and described herein. The invention is capable of other embodiments and of being practiced in various ways. It is also to be understood that the phraseology or terminology used herein is for the purpose of description and not limitation.

The present invention provides for the embedding of particles of a microporous solid material in larger particles of a mesoporous solid material. This can be carried out by extrusion of the micron-sized or submicron-sized particles of a zeolite or similar material with the 50 to 250 micron-sized particles of the mesoporous material. To further strengthen the extrudates, a binder such as bentonite clay may be used; however, the macropores of the clay do not have any influence on the diffusion of the reactant or product molecules, and thus do not affect the overall catalytic results of the hybrid catalyst.

As a result of the embedding of the zeolite particles in the cocatalyst ones, the micropore network of the zeolite and the mesopore system of the cocatalyst are so imbricated in each other that they form a pore continuum where diffusing molecules do not encounter any energy barrier similar to that which normally exists at the pore openings of the zeolite crystallite.

It is essential to note that the hybrid catalyst configuration is completely different from a mere mechanical mixture of two types of solid particles which may be in close contact (if the particles are extremely fine) but their external surfaces do not bind to each other to create conditions for strong synergistic interactions. With the hybrid catalyst configuration of the present invention, reaction products are more rapidly evacuated to the outside: this results in higher product yields and longer on-

stream catalyst stability. If the zeolite particles are used alone (self-bonded or bound through a macroporous binder or matrix), there is an energy barrier at the micropore mouth of the zeolite particle owing to the sudden change of the surface curvature at the rim of the opening, if a molecule has to diffuse from the zeolite micropore (very small radius of less than 2 nm) to the flat (external) surface of the zeolite particle (radius: infinity, see paper of Derouane et al, Journal of Catalysis 110 (1988) 58). In some acido-catalyzed reactions, bulky molecules like the condensed polyaromatics are produced: if they are not rapidly removed from the narrow pores of the zeolite, they undergo a transformation into coke which may deactivate the zeolite active surface or result in a pore blockage.

Therefore, the presence of a mesoporous irreducible or reducible oxide used as a cocatalyst in combination with a zeolite component, the whole assuming the configuration of the hybrid catalyst of this invention, enhances the yield of the desired product. Such a beneficial effect of the mesoporous cocatalyst is tentatively attributed to the formation of a "funnel-shaped" micropore-mesopore continuum which decreases the effect of the energy barrier at the pore openings of the zeolite crystallites. Examples 1 and 2 report such enhancements for two different catalytic reactions.

EXAMPLE 1

AROMATIZATION OF n-BUTANE WITH A HYBRID CATALYST CONTAINING AN IRREDUCIBLE OXIDE COCATALYST:

A ZSM-5 zeolite was synthesized according to U.S. Pat. No. 3,702,886, the disclosure of which is incorporated herein by reference. The composition of the

synthesis gel and the experimental parameters were selected so that the resulting zeolite had a Si/Al atomic ratio of 36.

The ZSM-5 zeolite was converted into the acid form (H-ZSM-5) by ion-exchange with a 5 wt % ammonium chloride solution followed by drying at 120 °C for 10 h and activating by calcination in air at 550 °C for 10h. The BET surface area was = 413 m^2/g. The Na_2O content was lower than 0.2 wt %. The average pore size was = 0.53 nm (microporous material). The average particle size is ca. 2-3 μm.

To prepare the final catalyst (referred to as H-ZSM5), the H-ZSM-5 (powder, 80 wt %) and bentonite (20 wt %) were mixed. Water was added dropwise to the mixture until a malleable paste was obtained. The latter was extruded into 1 mm O.D. extrudates.

The final catalyst was also prepared using a manual press for preparing the hybrid catalysts in the form of pellets: the results were similar to those obtained with the extrusion.

The resulting extruded or pelletized catalysts were then dried at 120 °C for 10 h and activated in air at 550 ° C for 10 h.

Ludox ™ colloidal silica was evaporated to dryness on a hot plate. The resulting solid (referred to as LuSi) was dried at 120 ° C for 10 h and activated at 550 ° C for 10 h. The BET surface area was = 105 m^2/g. The average pore size was = 12.5 nm (mesoporous material). The average particle size was = 200 μm.

Another cocatalyst used was the -alumina [Strem Chemicals; BET surface area = 146 m^2/g ; average pore size = 5.3 nm (mesoporous materials); average particle size = 150 μm, referred to as Al].

To prepare the final hybrid catalysts (referred to as H-ZSM-5/LuSi and H-ZSM-5/Al, respectively), the H-ZSM-5 (powder, 80 wt %), the LuSi or Al (powder, 16 wt %) and bentonite (powder, Anachemia, USP Lab-grade, 4 wt %) were mixed. These extrudates were thermally treated following the same procedure as described for the H-ZSM-5 catalyst.

The experimental setup was as follows: catalytic testing with n-butane (temperature 540 °C, weight hourly space velocity (WHSV) of 0.5 h^{-1}, weight of catalyst 4 g and duration of a run of 3.5 h).

In Table 1 are reported the catalytic activity of the H-ZSM-5, the H-ZSM-5/LuSi and the H-ZSM-5/Al samples. It was also shown in separate tests that bentonite clay alone did not give any significant conversion of n-butane under the same reaction conditions.

Table 1

Catalytic activity of the reference zeolite H-ZSM-5 and the hybrid catalyst containing the mesoporous cocatalyst

Catalyst	**H-ZSM-5**	**H-ZSM-5/LuSi**	**H-ZSM-5/Al**
Conversion (wt%)	81.5	92.5	94.7
Product selectivity (wt %)			
C_1-C_4 alkanes	55.3	44.6	53.7
C_2-C_4 alkenes	20.4	11.4	12.1
C_5^+ aliphatics	4.5	2.2	0.9
aromatics	19.9	41.8	33.3
aromatic yield (%)	16.2	38.7	31.5

Therefore, the hybrid catalyst configuration provides an aromatic yield which is significantly higher than that of the parent zeolite: equal to more than the double for the hybrid catalyst containing the LuSi.

EXAMPLE 2

SELECTIVE HYDROCRACKING OF n-OCTANE WITH A HYBRID CATALYST CONTAINING AN IRREDUCIBLE OXIDE COCATALYST:

The selective acido-catalyzed hydrocracking of n-octane was carried out using the Y-type zeolite [acid form obtained by calcining the NH_4-Y zeolite powder purchased from U.O.P. at 550 °C for 10 h; BET surface area = 610 m^2/g; pore size = 0.74 nm (microporous material); Si/Al = 2.7; average particle size = 15 μm]. Pt (0.5 wt %) was loaded into the zeolite by impregnation with an aqueous solution of tetraamine platinum (II) chloride. Pt was used to keep the zeolite surface clean from the coke normally formed during the hydrocracking reaction. The final extrudates of the reference zeolite (referred to as PtH-Y) were obtained by extrusion of a solid mixture of PtH-Y (powder, 70 wt %) and bentonite (30 wt %), and activated in the same way as for the catalysts of Example 1.

The alumina of Example 1 was used as a cocatalyst. The hybrid catalyst (referred to as PtH-Y/Al) was obtained by extrusion (and subsequent activation) of PtH-Y (70 wt %), Al (20 wt %) and bentonite (10 wt %).

The experimental set-up was identical to that used for Example 1. The reaction parameters were as follows: WHSV = 0.1 h^{-1}, temperature = 222 °C; weight of catalyst = 1.25 g; flow-rate of hydrogen = 12 ml/min; flow-rate of nitrogen = 16 ml/min. Prior to any catalytic testing, the catalyst was reduced in the presence of hydrogen (same hydrogen flow-rate as for the reaction) at 350 °C for 2 h.

In Table 2, it is seen that the conversion and the yield of cracking products were significantly higher for the hybrid catalyst. It was reported in separate tests that bentonite and alumina alone did not give any significant hydrocracking activity under the same reaction conditions.

Table 2

Hydrocracking of n-octane over parent PtH-Y and hybrid catalysts

Catalyst	PtH-Y	PtH-Y/Al
Conversion (wt %)	87.1	92.1
Yield of isobutane (wt %)	45.4	47.8
Yield of cracking products (wt %)	68.4	72.6

OTHER EXPERIMENTAL EVIDENCE OF THE INFLUENCE OF THE MESOPOROUS COCATALYST:

In the reaction of paraffin aromatization, other oxides were also investigated, which included various silicas, aluminas, aluminosilicas, MgO, TiO_2, ZrO_2, Fe_2O_3 and Cr_2O_3, some of them being not irreducible oxides. The yield of aromatics was significantly enhanced.

The preferred cocatalyst was the dried Ludox™ colloidal silica. It is theorized that the high performance of the LuSi cocatalyst results from the following properties:

i) network of mesopores contributing to the decrease (or suppression) of the energy barrier at the micropore openings of the zeolite particles;

ii) high surface area for better removal of reaction products; and

iii) malleability of the silica (large) particles during the extrusion process. This provides better embedding of the (much smaller) zeolite particles, thus decreasing the number and size of macropores which may be formed between the zeolite and the cocatalyst particles.

The bentonite clay used did not apparently intervene in the catalytic conversion. In fact, hybrid catalysts prepared by hot pressing the zeolite and the cocatalyst into pellets, and subsequently crushing/sieving these pellets, gave similar results as obtained with hybrid catalysts containing 4 wt % of bentonite.

In addition, if the cocatalyst has itself a catalytic function (provided by incorporated metal species, for instance) which can react with reactant molecules (inward diffusion) or intermediates of the reaction with zeolite active sites (outward diffusion), the performance of the hybrid catalyst is further enhanced. This is shown in Example 3.

EXAMPLE 3

AROMATIZATION OF n-BUTANE WITH A HYBRID CATALYST CONTAINING A SUPPORTED GALLIUM OXIDE COCATALYST:

The ZSM-5 zeolite was the same as in example 1. Gallium oxide was supported on two different oxides: 1) dried colloidal silica (LuSi), and 2) alumina (Al) both mentioned in example 1.

1) 2.3 g of gallium nitrate (13 H_2O, from Strem Chem.) were dissolved in 5 ml of water. This solution was added to 4.5 g of Ludox™ colloidal silica from Dupont Corp., and the resulting mixture was stirred for a few minutes. Then the water was gently evaporated to dryness on a hot plate. The resulting solid was further dried

at 120 °C for 10 h and activated in air at 550 ° C for 10 h. This cocatalyst will be referred to as Ga-LuSi.

2) 1.6 g of gallium nitrate were dissolved in 4.0 ml of water. This solution was added under gentle stirring to 1.3 g of alumina powder. The suspension was allowed to stand overnight at room temperature. The resulting wet solid was dried at 120 °C for 10 h and activated in air at 550 °C for 10 h. This cocatalyst will referred to as Ga-Al.

The hybrid catalysts (referred to as H-ZSM-5/Ga-LuSi and H-ZSM-5/Ga-Al, respectively) were prepared by admixing the respective cocatalysts (16 wt %) with H-ZSM-5 zeolite (80 wt %) and bentonite clay (4 wt %), and then extruded and thermally treated as in Example 1. The content of gallium oxide of the resulting hybrid catalysts was ca. 3 wt %.

Table 3 reports the catalytic data of the two hybrid catalysts obtained under the same experimental conditions as in Example 1.

Table 3

Catalytic results obtained with the hybrid catalysts containing gallium oxide supported on mesoporous solid oxides

Catalyst	**H-ZSM-5/Ga-LuSi**	**H-ZSM-5/Ga-Al**
Conversion (wt%)	99.6	98.3
Product selectivity (wt %)		
C_1-C_4 alkanes	28.8	45.2
C_2-C_4 alkenes	3.6	7.7
C_5^+ aliphatics	0.1	0.7
aromatics	67.5	46.4
aromatic yield	67.2	45.6

The comparison of the results of Table 1 with those of Table 3 shows that supported gallium oxide was capable of:

i) increasing the conversion of n-butane by converting some of the reactant molecules in their inward-diffusion or some of the unconverted ones in their outward-diffusion. In fact, one of the most demanding step in the aromatization reaction of a paraffin (n-butane in our case) over the strong acid sites of the zeolite, is the hydride abstraction resulting in an olefin which is the actual beginning of the aromatization sequence. The dehydrogenating properties of the supported gallium oxide produces more olefinic species, thus increasing further the conversion of n-butane;

ii) increasing the production of olefins by dehydrogenating the product paraffins in the outward-diffusion stream (decrease of the yield of light paraffins);

iii) increasing the production of aromatics from these olefins (and product olefins) and from the product naphthenic species (which are intermediates of the aromatization reaction of the olefins) coming from the zeolite micropores, with the following consequence: a significant decrease of the yields of light olefins and heavy aliphatics, and an important enhancement of the yield of aromatics.

The use of an "active" cocatalyst is also extremely beneficial to reactions which require several catalytic functions (polyfunctional catalytic systems), as shown in Example 4.

EXAMPLE 4

UPGRADING OF STEAM-CRACKING PRODUCTS:

Steam-cracking (of light paraffins, naphthas or heavy oils) is one of the most widely used basic petrochemical processes. It is used by industries to produce light olefins such as ethylene, propylene, butenes and butadiene and it is also relied upon for the production of aromatics such as benzene, toluene and xylenes (BTX). Since enormous quantities are processed throughout the world, even small yield improvements lead to substantial profit increases.

Pure or modified ZSM-5 zeolite, and other molecular sieve silicoaluminophosphates such as SAPO-34, can also lead to highly efficient production of light olefins from methanol. ZSM-5 zeolite and the hybrid catalyst containing a dehydrogenating cocatalyst were tested. The cocatalyst was obtained by impregnating an aqueous solution of chromium nitrate nonahydrate (Aldrich Chem.) onto the alumina of Example 1 which was pretreated with an aqueous solution of NaOH (0.1N, 10 ml/g, 1 hour at room temperature). The cocatalyst, dried (120°C for 10 h) and activated in air (550 °C for 10 h), contained 25 wt % of Cr_2O_3 and will be referred to as Cr-Al.

The experimental set-up comprises two reactors installed in series: Reactor I for steam-cracking and Reactor II for the catalytic up-grading reactions.

In Tables 4 and 5 are reported the yields of the products of steam-cracking of propane as analyzed at the exit of reactor I, the reaction being carried out at 780 °C and 800 °C, respectively as described in US Patent 4,732,881, the disclosure of which is hereby incorporated by reference. The reaction conditions were as follows: flow-rate of propane = 45 ml/min or 4.95 g/hour; flow-rate of steam = 1.7 g/hour; residence time = approximately 1 second (atmospheric pressure).

These products still in gaseous phase were intercepted by a catalytic reactor (Reactor II). Reactor II was set at 500 ° C and was loaded with a catalyst so that the weight hourly space velocity was equal to 1 h^{-1}.

The catalysts used in this series of tests were:

i) parent H-ZSM-5 zeolite of example 1;

ii) hybrid catalyst obtained by extrusion of the H-ZSM-5 zeolite (80 wt %) with the cocatalyst (Cr-Al, 16 wt %) and bentonite (4 wt %);

iii) hybrid catalyst obtained by extrusion of a ZSM-5 zeolite grown on asbestos and bearing some Zn^{2+} (1.0 wt % of ZnO incorporated by impregnation with an aqueous solution of Zn nitrate) with the cocatalyst Cr-Al (16 wt %) and bentonite (4 wt%). The latter hybrid catalyst will be referred to as HA-Zn/Cr-Al (see also US Patent 4,732,881).

Table 4

Catalytic up-grading of the products of propane steam-cracking at 780 ° C (Yields, propane conversion and aromatic content in wt %).

(*) = no catalyst in Reactor II.

Catalyst	**No(*)**	**H-ZSM-5**	**H-ZSM-5/Cr-Al**		**HA-Zn/Cr-Al**
Gaseous product yields (%):					
Ethylene	31.9	22.9	40.8		41.5
Propylene	11.8	12.1	12.1		11.4
Butenes, butadiene	3.4	8.7	3.2		2.9
ethane, butanes	16.3	15.1	10.8		10.5
propane	16.7	14.4	8.1	8.2	
methane	17.7	19.7	22.8	23.4	
liquid product yield	2.2	7.1	2.2	2.1	
aromatic content	0.0	26	45	57	
propane conversion	83.3	85.6	91.9		91.8
total olefin yield	47.1	43.7	56.1		55.8

Table 5

Catalytic up-grading of the products of propane steam-cracking at 800 ° C (Yields, propane conversion and aromatic content in wt %).

(*) no catalyst in Reactor II.

Catalyst	No(*)	H-ZSM-5	H-ZSM-5/Cr-Al		HA-Zn/Cr-Al
Gaseous product yields:					
ethylene	37.5	32.8	45.9		46.2
propylene, butenes	10.9	11.7	11.0		8.7
butadiene, ethane	3.5	6.3	3.1	3.2	
butanes	11.6	14.1	7.1	6.9	
propane	10.7	8.2	3.9	4.0	
methane	22.9	24.4	26.0	27.9	
liquid product yield	2.9	6.8	3.0	3.1	
aromatic content	42	64	70	73	
propane conversion	89.3	91.4	96.1	96.0	
total olefin yield	51.9	50.8	60.0	58.1	

It can be seen in Tables 4 and 5 that, with respect to the products of propane steam-cracking at 780 °C and 800 °C, and under the reaction conditions used for Reactor II:

i) the parent zeolite (acidic form) decreased mainly the yield of ethylene while it promoted a higher production of butenes and liquid products (with higher aromatic content). A slightly higher conversion of propane was also obtained.

ii) the use of the cocatalyst increased significantly the conversion of propane. Beside the strong dehydrogenating action of the cocatalyst which affects all the products coming from the zeolite micropores, a significant depolymerization effect is observed with respect to butenes/butadiene, and to heavy aliphatics. This can explain why

a much higher yield of ethylene was achieved with both hybrid catalysts.

Although the invention has been described above with respect with one specific form, it will be evident to a person skilled in the art that it may be modified and refined in various ways. It is therefore wished to have it understood that the present invention should not be limited in scope, except by the terms of the following claims.

I claim:

1. A hybrid catalyst suitable for the conversion of hydrocarbons and other organic compounds, said catalyst comprising 70 wt % to 85 wt % of microporous zeolite-type particles embedded in 10 wt % to 30 wt % of larger mesoporous solid particles, the latter being used as a cocatalyst.

2. The hybrid catalyst of claim 1, wherein the embedding of microporous particles in larger mesoporous particles involves the presence of up to 20 wt % of an inert clay binder.

3. The hybrid catalyst of claim 1, wherein the zeolite-type particles are particles having the ZSM-5 structure and in the acidic form.

4. The hybrid catalyst of claim 1, wherein the mesoporous solid particles used as a cocatalyst are particles of an oxide selected from the group consisting of silica, alumina, aluminosilica, magnesium oxide, titanium oxide, iron oxide, zirconium oxide, chromium oxide, nickel oxide, and mixtures thereof.

5. The hybrid catalyst of claim 4, wherein the mesoporous oxide acts as a support for a dehydrogenating species selected from a group consisting of gallium oxide, zinc oxide, manganese oxide, chromium oxide, molydennum oxide, tungsten oxide, a precious metal, a precious metal oxide, and mixtures thereof.

6. The hybrid catalyst of claim 5, wherein the precious metal species supported on the mesoporous oxide is a solid mixture of several metal species.

7. A method of making an hybrid catalyst wherein said hybrid catalyst is suitable for the conversion of hydrocarbons and other organic compounds, said catalyst comprising 70 wt % to 85 wt % of microporous zeolite-type particles embedded in 10 wt % to 30 wt % of larger mesoporous solid particles, the latter being used as a cocatalyst, said method comprising the steps of:

a) dry mixing said microporous zeolite-type particles with said larger mesoporous solid particles;

b) adding water dropwise to form of wet mass;

c) extruding said wet mass to provide an extrudate;

d) hot pressing said extrudate;

e) drying and activating said extrudate to obtain said hydrid catalyst.

8. The method of claim 7 wherein said zeolite-type particles have the ZSM-5 structure and the acidic form and wherein the mesoporous solid catalyst are particles of an oxide selected from the group consisting of silica, alumina, aluminosilica, magnesium oxide, titanium oxide, iron oxide, zirconium oxide, chromium oxide, nickel oxide, and mixtures thereof and wherein in step e) said drying is conducted at a temperature of at least about 120 °C and said activation is obtained at a temperature of at least about 550 °C.

9. The method of claim 8 wherein said drying is conducted for about at least 10 hours and said activation is conducted for at least about 10 hours.