

(43) International Publication Date
6 May 2010 (06.05.2010)(10) International Publication Number
WO 2010/051007 A1

PCT

(51) International Patent Classification:
C07C 2/68 (2006.01)(21) International Application Number:
PCT/US2009/005613(22) International Filing Date:
14 October 2009 (14.10.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
12/263,689 3 November 2008 (03.11.2008) US(71) Applicant (for all designated States except US): SAUDI
BASIC INDUSTRIES CORPORATION [SA/SA]; P.O.
Box 5101, Riyadh, 11422 (SA).

(72) Inventors; and

(75) Inventors/Applicants (for US only): GHOSH, Ashim,
Kumar [US/US]; 3418 Pine Brook Way, Houston, TX
77059 (US). KULKARNI, Neeta [US/US]; 2110 Dia-
mond Brook Dr., Houston, TX 77062 (US).(74) Agent: WHEELINGTON, Jimmy; SABIC Americas,
INC., SABIC Technology Center, 1600 Industrial Blvd.,
Sugar Land, TX 77478 (US).(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ,CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO,
DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP,
KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD,
ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI,
NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD,
SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT,
TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ,
TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,
MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM,
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

Published:

- with international search report (Art. 21(3))

(54) Title: STABLE SHAPE-SELECTIVE CATALYST FOR AROMATIC ALKYLATION AND METHODS OF USING AND PREPARING

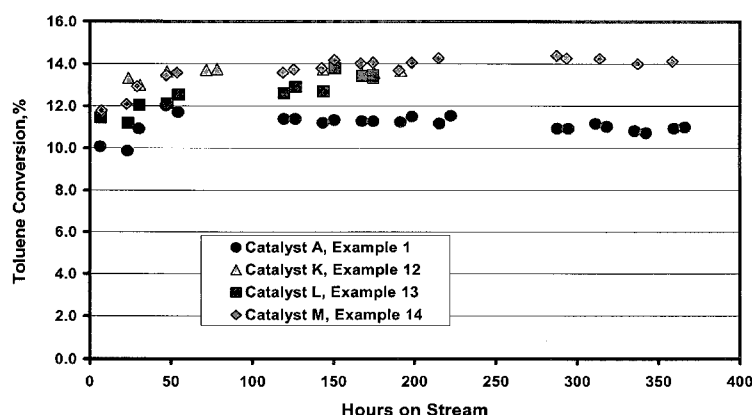


FIGURE 5

(57) Abstract: A catalyst and method of forming a catalyst for use in aromatic alkylation involves treating a zeolite, which may be a ZSM-5 zeolite, with a phosphorus-containing compound. The phosphorus-treated zeolite is combined with a binder material. The bound phosphorus-treated zeolite is treated with an aqueous solution of a hydrogenating metal compound by contacting the bound phosphorus-treated zeolite with the aqueous solution and separating the aqueous solution from the bound phosphorus-treated zeolite to form a hydrogenating-metal-containing zeolite catalyst. The catalyst may be used in preparing an alkyl aromatic product by contacting a hydrogenating-metal-containing zeolite catalyst with an aromatic alkylation feed of an aromatic compound and an alkylating agent under reaction conditions suitable for aromatic alkylation.

**STABLE SHAPE-SELECTIVE CATALYST FOR AROMATIC
ALKYLATION AND METHODS OF USING AND PREPARING**

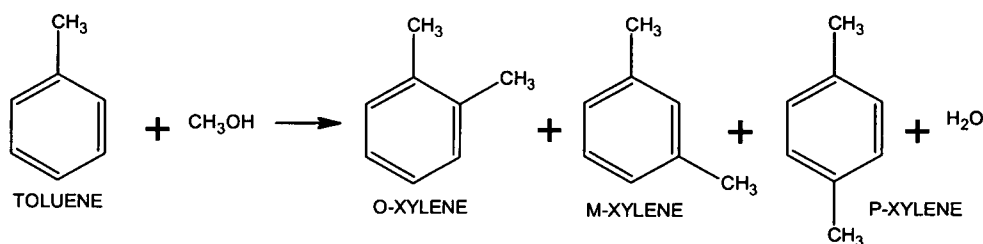
TECHNICAL FIELD

[0001] The invention relates generally to the alkylation of aromatic compounds and catalysts used for such reactions.

BACKGROUND

[0002] Aromatic compounds may be alkylated to form different alkylated aromatic products. One that has particular value is para-xylene. Para-xylene is a valuable substituted aromatic compound because of its great demand for its oxidation to terephthalic acid, a major component in forming polyester fibers and resins. It can be commercially produced from hydrotreating of naphtha (catalytic reforming), steam cracking of naphtha or gas oil, and toluene disproportionation.

[0003] Alkylation of toluene with methanol, which is also known as toluene methylation, has been used in laboratory studies to produce para-xylene. Toluene methylation has been known to occur over acidic catalyst, particularly over zeolite catalyst. In particular, ZSM-5 zeolite, zeolite Beta and silicaaluminophosphate (SAPO) catalysts have been used for this process. Generally, a thermodynamic equilibrium mixture of ortho (o)-, meta (m)- and para (p)-xylenes can be formed from the methylation of toluene, as is illustrated by the reaction below.



(1)

[0004] Thermodynamic equilibrium compositions of o-, m-, and p-xylenes may be around 25, 50 and 25 mole%, respectively, at a reaction temperature of about 500 °C. Such toluene methylation may occur over a wide range of temperatures, however. Para-xylene can be separated from mixed xylenes by a cycle of adsorption and isomerization. Byproducts such as C₉+ and other aromatic products can be produced by secondary alkylation of the xylene product.

[0005] A significantly higher amount of p-xylene can be obtained in toluene methylation reaction if the catalyst has shape selective properties. Shape selective properties can be obtained in modified zeolite catalysts by narrowing zeolite pore opening size, inactivation of the external surface of the zeolite or controlling zeolite acidity. Toluene methylation may occur over modified ZSM-5 zeolite catalysts giving

xylene products containing significantly greater amounts of p-xylene than the thermodynamic concentration.

[0006] Unfortunately, there are a number of technical hurdles for toluene methylation to be commercially successful. These include fast catalyst deactivation, low methanol selectivity, and so on. Most of the catalysts, if not all, for toluene methylation show fast catalyst deactivation. Typically, toluene conversion declines with time on stream due to rapid coke formation on the catalyst. The catalyst deactivation is one of the most difficult technical hurdles to overcome for commercial use of toluene methylation.

[0007] The present invention is directed to a catalyst and a method of preparation of a catalyst that has shape selective properties and that also has increased catalyst stability when used in aromatic alkylation reactions, such a toluene methylation.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] For a more complete understanding of the present invention, reference is now made to the following descriptions taken in conjunction with the accompanying figures, in which:

[0009] FIGURE 1 shows a plot of toluene conversion over time for toluene methylation reactions using Catalyst A (without metal) and Catalyst B (containing nickel) from Examples 1-3;

[0010] FIGURE 2 shows a plot of toluene conversion over time for toluene methylation reactions using Catalysts C-F (containing different amounts of nickel) from Examples 4- 7;

[0011] FIGURE 3 shows a plot of toluene conversion over time for toluene methylation reactions using Catalyst A (without metal) from Example 1 and Catalyst G (containing nickel) from Example 8;

[0012] FIGURE 4 shows a plot of toluene conversion over time for toluene methylation reactions using Catalyst H (self-bound P/ZSM-5 without metal) and Catalysts I and J (containing nickel) from Examples 9-11;

[0013] FIGURE 5 shows a plot of toluene conversion over time for toluene methylation reactions using Catalyst A (without metal) from Example 1 and Catalysts K-M (containing platinum) from Examples 12-14; and

[0014] FIGURE 6 shows a plot of toluene conversion over time for the toluene methylation reactions using Catalysts A (without metal) from Example 1 and Catalysts N-O (containing palladium) from Examples 15-16.

DETAILED DESCRIPTION

[0015] Zeolites are aluminosilicate materials having microporous structures. They may be naturally occurring or synthesized. Zeolites are commonly used as catalysts in a variety of different hydrocarbon conversion reactions such as isomerization and alkylation reactions. Among these is the alkylation of aromatic compounds.

[0016] The ZSM-5 zeolite is one of the most versatile zeolites used for catalyst in aromatic alkylation. Specific reference is made to the use of a ZSM-5 zeolite that has been modified in accordance with the invention for use in toluene methylation, for which the modified zeolite is particularly well suited. It will be apparent to those skilled in the art, however, that the zeolite catalysts described herein may have application for use in other types of reactions, such as transalkylation and other aromatic alkylation reactions. In particular, the catalyst of the invention may have application to reactions to provide increased selectivity for para-isomers in mixed dialkylated aromatic products.

[0017] The ZSM-5 zeolite is a porous material containing intersecting two-dimensional pore structure with 10-membered oxygen rings. Zeolite materials with such 10-membered oxygen ring pore structures are often classified as medium-pore zeolites. Such medium-pore zeolites typically have pore diameters ranging from 5.0 Å to 7.0 Å. The ZSM-5 zeolite is a medium pore-size zeolite with a pore diameter of from about 5.1 to about 5.6 Å.

[0018] Although specific reference and emphasis is made with respect to ZSM-5 zeolite, other zeolites may be treated and formed using the techniques described herein as well. One skilled in the art will therefore readily appreciate that other zeolite materials besides ZSM-5 zeolite may provide similar properties to those of the ZSM-5 zeolite materials described, such as mordenite, omega, etc. These may be medium pore zeolites as well.

[0019] The ZSM-5 zeolite catalysts and their preparation are described in U.S. Patent No. 3,702,886, which is herein incorporated by reference. The starting ZSM-5 may be an NH_4^+ or H^+ form and may contain traces of other cations. In the present invention, the ZSM-5 zeolite catalyst may have a silica/alumina molar ratio of from about 30 or lower to about 1000 or higher prior to modification, more particularly, the silica/alumina molar ratio may be from about 30, 50, 80, 100, 200, 250, 300, 400, 500

to about 1000 or more, including any and all data points within such range and the end points of the such range.

[0020] It should be understood that with respect to any concentration or amount range listed or described herein as being useful, suitable, or the like, it is intended to include every concentration or amount within the range, including the end points, and is to be considered as having been specifically stated. For example, "a range of from 1 to 10" is to be read as indicating each and every possible number along the continuum between about 1 and about 10. Thus, even if specific data points within the range, or even no data points within the range, are explicitly identified or refer to only a specific few, it is to be understood that the inventors appreciate and understand that any and all data points within the range are to be considered to have been specified, and that the inventors are in possession of the entire range and all points within the range.

[0021] To provide para-selective properties to the ZSM-5 zeolite or other zeolites, the zeolite is modified by treating it with phosphorus-containing compounds. Such phosphorus-containing compounds may include, but are not limited to, phosphonic, phosphinous, phosphorus and phosphoric acids, salts and esters of such acids and phosphorous halides. In particular, phosphoric acid (H_3PO_4) and ammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) may be used as the phosphorus-containing compound to provide a catalyst for aromatic alkylation or toluene methylation with shape selective properties to provide increased para-selectivity. Such modified catalysts may contain phosphorus (P) in an amount of from about 0.01 wt% to about 15 wt% by total weight of the catalyst.

[0022] The phosphorus treatment may be carried out by various techniques. This may include slurry evaporation, wet incipient and spray-dry methods. In slurry evaporation, the phosphorus may be incorporated into the catalyst by preparing a slurry of the zeolite and an aqueous solution of the phosphorus compound. Heating of the slurry may be used to facilitate treatment of the zeolite catalyst and to evaporate liquids. Heating of the slurry to temperatures of from about 25 °C or more, with from about 70 °C to about 100 °C may be suitable in most instances. The slurry may also be stirred or agitated during this step to ensure uniform treatment. The evaporation of the liquid from the zeolite slurry can be alternatively achieved by using a spray-dry technique which is well known in the art.

[0023] In the wet incipient method, an aqueous solution of the phosphorus compound is added, such as by spraying, to dry zeolite without forming a slurry. The dry zeolite, which may be initially in the form of a powder, may be mixed with the phosphorus compound or its aqueous solution. If necessary, water may be added to the mixture of zeolite powder and phosphorus containing compound or its solution to facilitate interaction between them. The phosphorus treated zeolite is then calcined using a temperature profile with a maximum temperature of from about 400 °C to about 700 °C. In some embodiments, the P-treated zeolite may be heated at a temperature of about 300 °C or higher prior to binding and then the zeolite is bound with a suitable binder, as described in U.S. Patent No. 7,368,410, which is herein incorporated by reference.

[0024] The phosphorus treated zeolite after calcination is combined with a binder material to form catalyst with a particular shape, for example, 1/16-inch diameter cylindrical shaped extruded catalyst. The binder materials may include inorganic oxide materials. In particular, a binder of an aluminum-containing material, such as alumina, clay, aluminum phosphate, silica-alumina or other-aluminum containing material, or their combinations, may be particularly useful. The bound catalyst may contain from about 1 wt% to about 99 wt% of binder material by total weight of the catalyst. In some applications the binder may be present in an amount of from about 10 wt% to about 50 wt% binder by total weight of catalyst.

[0025] Even without a binder the phosphorus treated zeolite (prior to calcination as described above) can also be formed into a particular shape and size as catalyst, for example, 1/16-inch diameter cylindrical shaped extrudates. Such catalyst may be described as "self-bound" catalyst.

[0026] The formed catalyst (either self-bound or bound with binder such as alumina) may then be calcined or heated at a temperature of about 400 °C or higher, more particularly at a temperature from about 450 °C to about 700 °C. Such heating may be carried out for 0.5 hours or more.

[0027] In order to provide increased catalyst activity or stability, the bound phosphorus-treated zeolite includes a hydrogenating metal. The hydrogenating metal may be any of the group VIIIA transition metals and may include nickel, palladium and platinum, as well as other metals. Nickel is particularly well suited as the hydrogenating metal. The hydrogenating metal may be present in an amount of from

about 0.01 weight % to about 5.0 weight %, more particularly, from about 0.03 weight % to about 2.0 weight % of the total weight of zeolite catalyst. The hydrogenating metal may be added to the catalyst as hydrogenating metal salt or other compound that readily dissolves in water.

[0028] Unexpectedly, the presence of a hydrogenating metal in a bound phosphorus-treated ZSM-5 zeolite catalysts has an impact on the activity of the final catalyst. A hydrogenating metal deposited on the bound phosphorus-treated zeolite provides increased activity. Deposition of the hydrogenating metal may be carried out by immersing the bound phosphorus-treated zeolite catalyst in an aqueous solution containing the hydrogenating metal. The temperature of the solution may be maintained at room temperature or a temperature below the boiling point of the solution. After a period of 5 min or more, the liquid is separated from the solid. This is done through decantation or filtration or other non-evaporative separation techniques for separating liquids from solids. As used herein, the term or expression "separation," "separating" or similar expressions as it is applied to the separation of the liquids and solids upon the treatment of the zeolite with an aqueous solution of a hydrogenating metal is meant to exclude evaporation of liquids from the solids. As is demonstrated in the examples, treatment of self-bound P/ZSM-5 catalyst with the hydrogenating metal solution did not result in a catalyst exhibiting the increased catalytic activity.

[0029] The method of treatment of the bound P/ZSM-5 catalyst with hydrogenating metal has an added impact on catalyst activity or stability as well. As demonstrated in the examples, the separation of liquid by filtration or decantation technique after treating the bound zeolite catalyst with solution containing hydrogenating metal resulted in a catalyst with further increased activity or stability than the commonly used impregnation technique where the liquid is evaporated to dryness. See, for example, Table 7: Catalyst G v. Catalyst E.

[0030] After treatment with the hydrogenating metal, the treated catalyst may be calcined at a temperature from about 400 °C to about 600 °C in an environment containing oxygen, typically air. The hydrogenating metal in the catalyst after such calcinations may be present in the oxide form, for example, Ni as NiO.

[0031] The hydrogenating metal loaded zeolite catalyst may be further pretreated prior to use in alkylation or other reactions to reduce or to lower the oxidation state of

the hydrogenating metal in a reducing environment. Such treatment includes contacting the catalyst with a reducing gas at an elevated temperature. The reducing gas may be hydrogen (H_2) or a hydrogen-containing gas, such as a mixture of hydrogen and nitrogen (N_2) or light alkane(s). The catalyst is contacted with the reducing gas, which may be mixed with an inert carrier gas, such as nitrogen at an initial starting temperature. The temperature may be slowly ramped up during the pretreatment, with the initial starting temperature being from about 100 to about 200 °C, and which may be increased at a rate of from about 0.2 to about 10.0 °C/min to the final pretreatment temperature. The final pretreatment temperature may be from about 350 to about 600 °C, more particularly from about 400 to about 550 °C. The pretreatment may be carried out from about 0.5 to 10 hours or more, more particularly from 1 to 9 hours, and still more particularly from about 2 to 7 hours.

[0032] Based on temperature programmed reduction profile data on NiO or the Ni^{2+} containing zeolite catalyst, it is believed that the above described catalyst pretreatment may cause reduction of Ni^{2+} to Ni^+ and Ni^0 . The hydrogenating metal ions to an oxidation state of less than 1 may be useful in retarding the coke formation during the alkylation reactions, and thus facilitate increasing the catalyst stability.

[0033] After reducing, the hydrogenating metal containing zeolite catalyst may also be steamed prior to use for the catalytic reactions. The catalyst may be steamed at a temperature of 300 °C or lower before using the catalyst in any reaction. The steaming can be carried out in-situ or ex-situ of the reactor. In some embodiments, the catalyst is steamed at mild temperatures. Methods for steaming at mild temperatures that are useful in the present invention are described in U.S. Patent No. 7,304,194, which is herein incorporated by reference.

[0034] After reducing and any steaming, the catalyst may be contacted with an appropriate feed under alkylation reaction conditions to carry out the aromatic alkylation. Examples of alkylation reactions for which the invention has application include toluene alkylation with an alkylating agent such as methanol. Other examples may include gas phase toluene disproportionation in the presence of hydrogen producing benzene and mixed-xylenes. While the invention has application to many aromatic alkylation reactions, it is particularly well suited for toluene methylation to produce para-xylene using ZSM-5 zeolite catalyst. Although much of the description

herein may be directed to such toluene methylation, it will be readily understood by those skilled in the art that it is not solely limited to such use.

[0035] The hydrogenating metal containing zeolite catalyst may be contacted with an appropriate feed of an aromatic hydrocarbon and an alkylating agent under alkylation reaction conditions to carry out aromatic alkylation. In aromatic alkylation an "alkylation feed" feed may be used. A gas cofeed may also be used. The cofeed gas may include hydrogen or an inert gas. As used herein, the expression "alkylation feed" is meant to encompass the aromatic compound and the alkylating agent. As used herein with respect to toluene methylation, the expression "methylation feed" is meant to encompass the feed of toluene and methanol.

[0036] In addition to any cofeed gas, water that may be in the form of steam, may also be introduced into the reactor as cofeed along with the alkylation feed. The water or steam used for the alkylation or methylation reaction may be introduced, with or without hydrogen or inert gas as cofeed, with the alkylation feed to the reactor during the start up of the alkylation reaction, or it may be introduced subsequent to initial start up. In either case, liquid water may be added and vaporized prior to its mixing with cofeed gas (if any) and the alkylation feed. The use of water cofeed in aromatic alkylation is described in U.S. Patent No. 7,060,864, which is hereby incorporated by reference.

[0037] The reactor pressure for toluene methylation or other aromatic alkylation may vary, but typically ranges from about 10 to about 1000 psig. Reactor temperatures may vary, but typically range from about 400 to about 700 °C. Upon introduction of feed into the reactor, the catalyst bed temperature may be adjusted to a selected reaction temperature to effect a desired conversion. The temperature may be increased gradually at a rate of from about 0.1 °C/min to about 10 °C/min to provide the desired final reactor temperature. As used in the examples, reactor temperature refers to the temperature as measured at the inlet of catalyst bed of the reactor.

[0038] The reaction may be carried out in a variety of different reactors that are commonly used for carrying out aromatic alkylation reactions. Single or multiple reactors in series and/or parallel may be suitable for carrying out the aromatic alkylation or toluene methylation reactions.

[0039] As used herein, catalytic activity can be expressed as the % moles of the hydrocarbon or reactant converted with respect to the moles of hydrocarbon or

reactant fed. In toluene methylation where toluene is converted to xylenes, the catalytic activity may be measured by the toluene converted with respect to the moles of toluene fed and can be defined by the following formulas:

$$\text{Mole\% Toluene Conversion} = [(T_i - T_o)/T_i] \times 100 \quad (2)$$

where, T_i is the number of moles of toluene fed and T_o is the number of moles toluene unreacted. As used herein, selectivity for mixed xylenes may be expressed as:

$$\text{Mole\% Mixed Xylene Selectivity} = [X_{tx}/(T_i - T_o)] \times 100 \quad (3)$$

where, X_{tx} is the number of moles of total or mixed (o-, m- or p-) xylenes in the product.

As used herein, selectivity for p-xylene may be expressed as:

$$\text{Mole\% p-Xylene Selectivity} = (X_p/X_{tx}) \times 100 \quad (4)$$

where, X_p is the number of moles of p-xylene.

As used herein, methanol conversion may be expressed as:

$$\text{Mole \% Methanol Conversion} = [(M_i - M_o)/M_i] \times 100 \quad (5)$$

where, M_i is the number of moles of methanol fed and M_o is the number of moles methanol unreacted.

As used herein, methanol selectivity for toluene methylation may be expressed as:

$$\text{Mole\% Methanol Selectivity} = [X_{tx}/(M_i - M_o)] \times 100 \quad (6)$$

where, X_{tx} is the number of moles of mixed (o-, m- or p-) xylenes, M_i is the number of moles of methanol fed and M_o is the number of moles of unreacted methanol.

[0040] The following examples better serve to illustrate the invention.

EXAMPLES

EXAMPLE 1

Comparative Catalyst A

[0041] A NH_4 -ZSM-5 zeolite powder having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of between 250 and 300 was treated with H_3PO_4 and then was calcined at a temperature of about 530 °C. The phosphorus treated ZSM-5 zeolite was crushed into fine powder and was then combined with about 20% by weight of alumina binder and extruded into 1/16-inch diameter cylindrical shaped catalyst extrudates. The bound zeolite was then calcined or heated to a temperature of 530 °C. The powdered phosphorus treated ZSM-5 (P/ZSM-5) and the alumina bound P/ZSM-5 catalyst (Catalyst A) were analyzed for Na_2O , P_2O_5 , SiO_2 and Al_2O_3 by X-ray fluorescence (XRF), and for BET surface area and total pore volume by N_2 adsorption. The results are shown in Table 1 below.

Table 1

	Elemental Analysis, wt%				N_2 Adsorption	
	Na_2O	P_2O_5	SiO_2	Al_2O_3	SA, m^2/g	N_2 PV, cc/g
Powdered P/ZSM-5	<0.04	21.6	79.2	0.5	211	0.13
Catalyst A	<0.04	17.2	63.4	20.4	243	0.17

[0042] Catalyst A, described above, was tested for toluene methylation reaction in a fixed bed, continuous flow type reactor. A catalyst charge of 5.4 ml (catalyst size: 20-40 mesh) was loaded in the reactor. The catalyst was dried by slowly raising the catalyst bed temperature (about 5 °C/min) to 150 °C under hydrogen flow (200 cc/min) for about one hour. The catalyst was further heated at 480 °C for 3 hours under H_2 flow (same flow rate). The catalyst was steamed by introducing water vapor (2.2 mmole/min) with a carrier gas of H_2 (459 cc/min) at 200 °C overnight. A premixed toluene and methanol feed (molar ratio 4.5) was added to the reactor at 200 °C. The liquid hourly space velocity (LHSV) [based on methylation feed (toluene+methanol)] was maintained at about 2 hr^{-1} and a cofeed of H_2 gas was fed and maintained to provide a H_2 /methylation feed molar ratio of about 7-8. In addition, water was added to the reactor as cofeed and was vaporized prior to introduction to the reactor. The H_2O /methylation feed molar ratio was about 0.8 and

the reactor inlet pressure was about 20 psig. The catalyst bed inlet temperature was increased to 450 °C and then adjusted to 485 °C, at which toluene conversion was about 11.4 mole%. Reactor streams were analyzed to calculate conversion and selectivity.

[0043] Figure 1 shows toluene conversion for Catalyst A at different times on stream during a test period of about 365 hour. The reactor temperature was kept unchanged at catalyst bed inlet temperature of about 485 °C and average bed temperature of about 494 °C. Toluene conversion was found to decline with time on stream at a constant catalyst bed inlet temperature. This decline in conversion per unit time is the deactivation rate and it is estimated to be -0.065% per 24 hours. Table 2 shows toluene conversion, methanol conversion, toluene selectivity for mixed xylenes, para-xylene selectivity and methanol selectivity to mixed xylenes for Catalyst A.

Table 2

Example#	Catalyst Description				Performance Test						
	Catalyst	Base Catalyst	Metal	Method	Drying Temp/°C	T/°C	X _{Tol}	X _{MeOH}	S _{MX}	S _{PX}	S _{MeOH}
1	Catalyst A	Al ₂ O ₃ -P/ZSM-5	0	"As-is"	480	485	11.4	96	97.8	96.6	53.8
2-3	Catalyst B	Al ₂ O ₃ -P/ZSM-5 (Catalyst A)	0.07% Ni	Aged & Decanted	430	488	15.4	100	96.5	90.3	70
					480	485	15.4	100	97.0	91.6	73
4	Catalyst C	Al ₂ O ₃ -P/ZSM-5 (Catalyst A)	0.03% Ni	Aged & Decanted	480	486	14.9	100	96.7	87.2	65.8
5	Catalyst D	Al ₂ O ₃ -P/ZSM-5 (Catalyst A)	0.04% Ni	Aged & Decanted	480	486	14.4	100	95.4	87.5	62.6
6	Catalyst E	Al ₂ O ₃ -P/ZSM-5 (Catalyst A)	0.09% Ni	Aged & Decanted	480	486	14.9	100	96.1	85.5	65.6
7	Catalyst F	Al ₂ O ₃ -P/ZSM-5 (Catalyst A)	0.15% Ni	Aged & Decanted	480	485	14.7	100	96.9	90.8	65
8	Catalyst G	Al ₂ O ₃ -P/ZSM-5 (Catalyst A)	0.10% Ni	Impregnated	480	485	13.5	100	97.9	95.1	60
9	Catalyst H	P/ZSM-5	0	"As-is"	480	496	17.7	91	95.3	86.4	57
10	Catalyst I	P/ZSM-5 (Catalyst H)	0.08% Ni	Aged & Decanted	480	498	12.7	86	97.3	96.1	45
11	Catalyst J	P/ZSM-5 (Catalyst H)	0.25% Ni	Aged & Decanted	480	497	8.4	79	96.2	91.9	34

X_{Tol} = Toluene conversion, mole%; X_{MeOH} = Methanol conversion, mole%; S_{MX} = Toluene selectivity to mixed-Xylene; S_{PX} = p-xylene selectivity, S_{MeOH} = Methanol selectivity to mixed-xylenes

EXAMPLE 2**Catalyst B**

[0044] Nickel was incorporated with the alumina bound P/ZSM-5 zeolite catalyst (Catalyst A) from Example 1 to form Catalyst B. Weighted 0.737 g of nickel hexahydrate was dissolved in 100 ml deionized water in a flask and 30.03 g extrudates of Catalyst A was immersed in the nickel salt solution in the flask which was then shaken for 5 minutes and was aged at 60 °C overnight. Catalyst A was then separated by decanting the liquid. The nickel-treated zeolite was then calcined at a maximum temperature of about 530 °C for 10 hours. The nickel content of the catalyst was 0.07 wt% by total weight as measured by XRF analysis. Catalyst preparation and analysis for Catalyst B are summarized in Table 3.

[0045] Catalyst B, described above, was tested for toluene methylation reaction in a fixed bed, continuous flow type reactor. A catalyst charge of 5.4 ml (catalyst size: 20-40 mesh) was loaded in the reactor. The catalyst was dried by slowly raising the catalyst bed temperature (about 5 °C/min) to 150 °C under hydrogen flow (200 cc/min) for at least one hour. The catalyst was further heated (reduced) at 430 °C for 3 hours under H₂ flow (same flow rate). The catalyst was steamed by introducing water vapor (2.2 mmole/min) with a carrier gas of H₂ (459 cc/min) at 200 °C overnight. A premixed toluene and methanol feed (molar ratio 4.5) was added to the reactor at 200 °C. The liquid hourly space velocity (LHSV) [based on methylation feed (toluene +methanol)] was maintained at about 2 hr⁻¹ and a cofeed of H₂ gas was fed and maintained to provide a H₂/methylation feed molar ratio of about 7-8. In addition, water was added to the reactor as cofeed and was vaporized prior to introduction to the reactor. The H₂O/methylation feed molar ratio was about 0.8 and the reactor pressure was about 20 psig and the catalyst bed inlet temperature was increased to 450 °C and then adjusted to 495 °C at which toluene conversion was about 15.4 mole%. Reactor streams were analyzed to calculate conversion and selectivity.

Table 3

Catalyst	(Extruded) Base Catalyst, g	Ni Salt, g	Water, ml	Aging Temp	Liquid Removal, Calcination	Wt% Ni by XRF
Catalyst A	Base Catalyst	N/A	N/A	N/A	N/A	N/A
Catalyst B	30.025	0.737	100	60 °C	Decanted & Calcined at 530 °C	0.07
Catalyst C	30.107	0.247	100	60 °C	Decanted & Calcined at 530 °C	0.03
Catalyst D	30.154	0.247	100	60 °C	Decanted & Calcined at 530 °C	0.04
Catalyst E	30.049	1.106	100	60 °C	Decanted & Calcined at 530 °C	0.09
Catalyst F	30.070	1.477	100	60 °C	Decanted & Calcined at 530 °C	0.15
Catalyst G	30.367	0.153	100	90 °C	Evaporated, Calcined at 530 °C	0.10

Base Catalyst = Alumina Bound P/ZSM-5 Extruded Catalyst

[0046] Figure 1 shows toluene conversion for Catalyst B, which was prereduced at 430 °C, at different times on stream during a test period of about 893 hours. The reactor temperature was kept unchanged at a catalyst bed inlet temperature of about 487 °C and average bed temperature of about 496 °C. The toluene conversion remained unchanged or somewhat increased during the test period at constant temperature showing catalyst stability. In other words, catalyst deactivation was not observed for Catalyst B during the 893 hour test run. The carbon (C) content on the spent catalyst was 2.3 wt%. Table 2 shows toluene conversion, methanol conversion, toluene selectivity for mixed xylenes, para-xylene selectivity and methanol selectivity to mixed xylenes for Catalyst B.

EXAMPLE 3

[0047] As in Example 2, Catalyst B was employed in toluene methylation. The reactor, catalyst loading, drying and steaming conditions were the same as in Example 2, except the catalyst was heated at a pre-reduction temperature of about 480 °C instead of 430 °C under H₂ flow prior to steaming.

[0048] Figure 1 shows toluene conversion at different times on stream during test period of 414 hours. The reactor temperature was kept unchanged at a catalyst bed inlet temperature of about 485 °C and the average bed temperature was about 493 °C

at which toluene conversion was about 15.4 mole%. The toluene conversion remained unchanged or somewhat increased during the test period at constant temperature showing catalyst stability. That is, the catalyst deactivation was not observed for Catalyst B during the 414 hour test period. The carbon (C) content on the spent catalyst was 3.4 wt%. Table 2 shows toluene conversion, methanol conversion, toluene selectivity for mixed xylenes, para-xylene selectivity and methanol selectivity to mixed xylenes for Catalyst B that was prereduced at 480 °C.

EXAMPLE 4-7

Catalysts C-F

[0049] In addition to Catalyst B, several nickel-loaded catalysts with different nickel contents were tested in toluene methylation reactions to examine the effects of Ni content on catalyst activity, selectivity and stability. Ni loaded catalysts C, D, E and F were made using base Catalyst A and the same procedure as described for Catalyst B above. Table 3 shows the amounts of base catalyst, nickel salt, amount of water used, aging temperature and nickel content (measured by XRF) on the final catalysts. The Ni contents in the catalysts varied from 0.03 wt% to about 0.15 wt%.

[0050] Catalysts C, D, E and F were tested in toluene methylation reactions. Catalyst loading, predrying, steaming and testing conditions were the same as described for Example 3. Figure 2 shows toluene conversions at different times on stream over Catalysts C, D, E and F. Table 2 summarizes toluene conversion, methanol conversion, toluene selectivity for mixed xylenes, para-xylene selectivity and methanol selectivity to mixed xylenes for Catalysts C, D, E and F.

[0051] Catalysts B, C, D, E and F showed an increased catalyst activity showing higher toluene conversion compared to Catalyst A (Table 2, Examples 1-7).

EXAMPLE 8

Catalyst G

[0052] In this example, an impregnation technique was used to form a Ni loaded catalyst (Catalyst G). In this technique, nickel was incorporated with the alumina bound P/ZSM-5 zeolite catalyst from Example 1 (Catalyst A). Nickel hexahydrate in an amount of 0.153 g was dissolved in 100 ml deionized water. The nickel salt

solution was added to 30.4 g of the extruded Catalyst A in a ceramic bowl and aged at 90 °C overnight. Most of the liquid was evaporated and further evaporation continued during calcination at 530 °C.

[0053] Catalyst G was then used in toluene methylation, as in the previous examples. A catalyst charge of 5.4 ml (catalyst size: 20-40 mesh) was loaded in the reactor. The catalyst was dried by slowly raising the catalyst bed temperature (about 5 °C/min) to 150 °C under hydrogen flow (200 cc/min) for at least one hour. The catalyst was further heated (reduced) at 480 °C for 3 hours under H₂ flow (same flow rate). The catalyst was steamed by introducing water vapor (2.2 mmole/min) with a carrier gas of H₂ (459 cc/min) at 200 °C overnight. A premixed toluene and methanol feed (molar ratio 4.5) was added to the reactor at 200 °C. The liquid hourly space velocity (LHSV) [based on methylation feed (toluene+methanol)] was maintained at about 2 hr⁻¹ and a cofeed of H₂ gas was fed and maintained to provide a H₂/methylation feed molar ratio of about 7-8. In addition, water was added to the reactor as cofeed and was vaporized prior to introduction to the reactor. The H₂O/methylation feed molar ratio was about 0.8 and the reactor pressure was about 20 psig and the catalyst bed inlet temperature was increased to 450 °C and then adjusted to about 485 °C (average catalyst bed temperature 498 °C). Reactor streams were analyzed to calculate conversion and selectivity.

[0054] Figure 3 shows catalyst activity as measured by toluene conversion at different time on stream over Catalyst G. For comparison toluene conversions obtained on Catalyst A are shown in Figure 3. Also Table 2 shows toluene conversion, methanol conversion, toluene selectivity for mixed xylenes, para-xylene selectivity and methanol selectivity to mixed-xylenes for Catalyst G. Catalyst G showed higher activity than Catalyst A (without metal) but showed lower activity than Catalyst E (Example 5) which had roughly the same nickel content, but the procedure for Ni loading used non-evaporative separation of liquids and solids.

EXAMPLE 9-11

Comparative Catalysts H-J

[0055] A "self-bound" P/ZSM-5 extruded catalyst was made by treating a NH₄-ZSM-5 zeolite powder having a SiO₂/Al₂O₃ mole ratio of between 250 and 300 with H₃PO₄ and made into an extrudable mixture, which was then extruded into 1/16-inch

diameter cylindrical shaped extrudates. The extruded catalyst was then calcined or heated to a maximum temperature of 530 °C. This formed Catalyst H. XRF analysis showed Catalyst H had the following composition: SiO₂ 77.65 wt%, Al₂O₃ 0.53 wt%, P₂O₅ 19.53 wt%, Na₂O <0.04 wt%. BET (N₂ adsorption) surface area and total pore volume of Catalyst H were 168 m²/g and 0.12 cc/g, respectively.

[0056] Several nickel loaded catalysts (I and J) were made using Catalyst H by treating it with different amounts of nickel using the same procedure as used for Catalysts B-F (see Table 4). The nickel contents of the Catalysts I and J were 0.08 wt% and 0.25 wt%, respectively, by total weight of catalyst.

Table 4

Catalyst	(Extruded) Base Catalyst, g	Ni Salt, g	Water, ml	Aging Temp	Liquid Removal, Calcination	Wt% Ni by XRF
Catalyst H	Base Catalyst	N/A	N/A	N/A	N/A	N/A
Catalyst I	32.093	0.323	100	60 °C	Decanted & Calcined at 530 °C	0.08
Catalyst J	32	0.739	100	60 °C	Decanted & Calcined at 530 °C	0.25

Base Catalyst = Self Bound P/ZSM-5 Extruded Catalyst

[0057] Catalysts H, I and J were tested for toluene methylation reaction. Catalyst loading, predrying under H₂ flow and steaming conditions were the same as described for Example 3. After the catalyst drying at 480 °C and steaming at 200 °C overnight, a premixed toluene and methanol feed (molar ratio 3.0) was added to the reactor at 200 °C. The liquid hourly space velocity (LHSV) [based on methylation feed (toluene+methanol)] was maintained at about 2 hr⁻¹ and a cofeed of H₂ gas was fed and maintained to provide a H₂/methylation feed molar ratio of about 7-8. In addition, water was added to the reactor as cofeed and was vaporized prior to introduction to the reactor. The H₂O/methylation feed molar ratio was about 0.8 and the reactor pressure was about 20 psig and the catalyst bed inlet temperature was increased to 450 °C and then adjusted to about 485 °C. Reactor streams were analyzed to calculate conversion and selectivity.

[0058] Figure 4 shows toluene conversions at different time on stream for Catalysts H, I and J. Table 2 shows toluene conversion, methanol conversion, toluene

selectivity for mixed xylenes, para-xylene selectivity and methanol selectivity to mixed xylenes for Catalysts H, I and J. Catalyst H, which was a self-bound P/ZSM-5 catalyst, showed toluene conversion of nearly 18 mole%, and toluene conversion declined slowly with time at a rate of -0.014% per 24 hours. Catalyst I, which contained about 0.08 wt% Ni, showed about 12.7 % toluene conversion, which declined at a rate of about -0.170% per 24 hour. Catalyst J, which contained about 0.25 wt% Ni, showed significantly lower toluene conversion initially and reached about 9% toluene conversion. The run was discontinued because of the low activity, and the deactivation rate was not estimated.

[0059] In summary, the addition of Ni on self-bound P/ZSM-5 did not show increased catalyst activity or improved catalyst stability. This is in contrast to those with the addition of Ni on alumina bound P/ZSM-5 catalysts.

EXAMPLE 12-14

Catalysts K-M

[0060] Pt-loaded P/ZSM-5 catalysts were made by adding various amounts of Pt on alumina bound P/ZSM-5 catalyst (Catalyst A) using the same procedure as used for Catalysts C, D, E and F. Catalyst A, described previously, was loaded with different loadings of platinum at 0.05, 0.11 and 0.18 wt% to form Catalysts K, L and M, respectively (see Table 5). The platinum was incorporated with the alumina bound P/ZSM-5 zeolite catalyst (Catalyst A) by dissolving different amounts of tetraamineplatinum (II) nitrate in about 100 ml of deionized water. Catalyst A (extrudates) was immersed in the platinum salt solution in a flask which was then shaken for 5 minutes and was aged at 60 °C overnight. Catalyst extrudate was separated from the aqueous liquid by decanting the liquid. The platinum-treated zeolites were then calcined at a maximum temperature of about 530 °C for 10 hours.

Table 5

Catalyst	(Extruded) Base Catalyst, g	Metal Salt, g	Water, ml	Aging Temp	Liquid Removal, Calcination	Wt% Metal by XRF
Catalyst A	Base Catalyst	N/A	N/A	N/A	N/A	N/A
Catalyst K	30.582	0.095	100	60 °C	Decanted & Calcined at 530 °C	0.05% Pt
Catalyst L	30.403	0.155	100	60 °C	Decanted & Calcined at 530 °C	0.11% Pt
Catalyst M	30.088	0.305	100	60 °C	Decanted & Calcined at 530 °C	0.18% Pt
Catalyst N	30.407	1.622	100	60 °C	Decanted & Calcined at 530 °C	0.05% Pd
Catalyst O	30.105	3.245	100	60 °C	Decanted & Calcined at 530 °C	0.09% Pd

Base Catalyst = Alumina Bound P/ZSM-5 Extruded Catalyst

[0061] Each of Catalysts K, L and M were tested in toluene methylation reactions. Catalyst loading, heating under H₂ flow and steaming conditions were the same as described for Catalyst B in Example 3. After the catalyst drying at 480 °C and steaming at 200 °C overnight, a premixed toluene and methanol feed (molar ratio 4.5) was added to the reactor at 200 °C. The liquid hourly space velocity (LHSV) [based on methylation feed (toluene+methanol)] was maintained at about 2 hr⁻¹ and a cofeed H₂ gas was fed and maintained to provide a H₂/methylation feed molar ratio of about 7-8. In addition, water was added to the reactor as cofeed and was vaporized prior to introduction to the reactor. The H₂O/methylation feed molar ratio was about 0.8 and the reactor pressure was about 20 psig and the catalyst bed inlet temperature was increased to 450 °C and then adjusted to about 485 °C. Reactor streams were analyzed to calculate conversion and selectivity.

[0062] Figure 5 shows the comparison of toluene conversion using Catalysts K-M containing different amounts of platinum and Catalyst A containing no metal. Table 6 shows toluene conversion, methanol conversion, toluene selectivity for mixed xylenes, para-xylene selectivity and methanol selectivity to mixed xylenes for Catalysts A and K-M. Compared to Catalyst A, all three platinum-containing Catalysts K, L and M showed increased catalyst activity showing higher toluene conversions and showed no apparent decline in toluene conversion during the test period.

Table 6

Example#	Catalyst Description				Performance Test						
	Catalyst	Base Catalyst	Metal	Method	Drying Temp/°C	T/°C	X _{Tol}	X _{MeOH}	S _{MX}	S _{PX}	S _{MeOH}
1	Catalyst A	Al ₂ O ₃ -P/ZSM-5	0	"As-is"	480	485	11.5	96	97.8	96.6	53.8
12	Catalyst K	Al ₂ O ₃ -P/ZSM-5 (Catalyst A)	0.05% Pt	Aged & Decanted	480	486	13.9	96.6	96.2	90.7	62.7
13	Catalyst L	Al ₂ O ₃ -P/ZSM-5 (Catalyst A)	0.11% Pt	Aged & Decanted	480	486	13.5	97.3	98.3	91.2	62.3
14	Catalyst M	Al ₂ O ₃ -P/ZSM-5 (Catalyst A)	0.18% Pt	Aged & Decanted	480	486	14.5	97.3	98.3	90.4	63.0
15	Catalyst N	Al ₂ O ₃ -P/ZSM-5 (Catalyst A)	0.05% Pd	Aged & Decanted	480	485	14.0	100	97.2	90.2	61.9
16	Catalyst O	Al ₂ O ₃ -P/ZSM-5 (Catalyst A)	0.09% Pd	Aged & Decanted	480	486	13.6	100	97.7	91.5	60.7

X_{Tol} = Toluene conversion, mole%; X_{MeOH} = Methanol conversion, mole%; S_{MX} = Toluene selectivity to mixed-Xylene; S_{PX} = p-xylene selectivity, S_{MeOH} = Methanol selectivity to mixed-xylenes

EXAMPLE 15-16**Catalysts N-O**

[0063] Pd-loaded P/ZSM-5 catalysts were made by adding various amounts of Pd on alumina bound P/ZSM-5 catalyst (Catalyst A) using the same procedure as used for Catalysts C, D, E and F. Catalyst A, described previously, was loaded with different loadings of palladium at 0.05 and 0.09 wt% to form Catalysts N and O, respectively (see Table 5). The palladium was incorporated with the alumina bound P/ZSM-5 zeolite catalyst (Catalyst A) by dissolving different amounts of palladium nitrate in about 100 ml of deionized water. Catalyst A (extrudates) was immersed in the palladium salt solution in a flask, which was then shaken for 5 minutes and was aged at 60 °C overnight. Catalyst extrudate was separated from the aqueous liquid by decanting the liquid. The palladium loaded catalysts were then calcined at a maximum temperature of about 530 °C for 10 hours.

[0064] Each of Catalysts N and O were tested in toluene methylation reactions. Catalyst loading, heating under H₂ flow and steaming conditions were the same as described for Catalyst B in Example 3. After treating the catalyst under H₂ flow at 480 °C for 3 hours and steaming at 200 °C overnight, a premixed toluene and methanol feed (molar ratio 4.5) was added to the reactor at 200 °C. The liquid hourly space velocity (LHSV) [based on methylation feed (toluene+methanol)] was maintained at about 2 hr⁻¹ and a cofeed H₂ gas was fed and maintained to provide a H₂/methylation feed molar ratio of about 7-8. In addition, water was added to the reactor as cofeed and was vaporized prior to introduction to the reactor. The H₂O/methylation feed molar ratio was about 0.8 and the reactor pressure was about 20 psig and the catalyst bed inlet temperature was increased to 450 °C and then adjusted to about 485 °C. Reactor streams were analyzed to calculate conversion and selectivity.

[0065] Table 6 shows toluene conversion, methanol conversion, toluene selectivity for mixed xylenes, para-xylene selectivity and methanol selectivity to mixed xylenes for Catalysts A and N-O. Figure 6 shows the comparison of toluene conversion using Catalysts N and O containing palladium and Catalyst A containing no metal. Compared to Catalyst A, both the palladium-containing Catalysts N and O showed

increased catalyst activity with higher toluene conversions and showed no apparent decline in toluene conversion during the test period.

[0066] Table 7 shows the comparison of toluene conversion and catalyst deactivation rate (toluene conversion decline rate per 24 hours at constant catalyst bed inlet temperature) between Catalyst A (no metal), Catalyst G (0.10 wt% Ni), Catalyst E (0.09 wt% Ni), Catalyst L (0.11 wt% Pt), Catalyst O (0.09 wt% Pd) having almost the same amount of metal on base Catalyst A. Catalyst G was made using the commonly used impregnation technique (evaporated the solution) and showed an increased toluene conversion compared to base Catalyst A (13.5% for Catalyst G versus 11.5% for Catalyst A, which is about a 17% relative increase in activity). Catalyst G also showed improved deactivation rate (-0.012% for Catalyst G versus -0.065% for Catalyst A). Whereas Catalyst E, which was made by decanting Ni salt solution, showed a further increased toluene conversion (14.9% for Catalyst E versus 11.5% for Catalyst A and 13.5% for Catalyst G) and toluene conversion did not decline during the testing period. Catalyst L (0.11 wt% Pt) and Catalyst O (0.09 wt% Pd) made by using the same method as used for Catalyst E (0.09% Ni) showed increased activity compared to base Catalyst A but not as much as for Catalyst E. Like Catalyst E, Catalysts L and O showed no decline in toluene conversion during the testing period.

Table 7

Catalyst Description				Performance Test		
Catalyst	Base	Metal	Method	X _{Tol}	Relative Activity Increase ¹	Deactivation Rate ²
Catalyst A	Al ₂ O ₃ -P/ZSM-5 (Catalyst A)	0	"As-is"	11.5	Base Case	-0.065
Catalyst G	Al ₂ O ₃ -P/ZSM-5 (Catalyst A)	0.10% Ni	Impregnated	13.5	17%	-0.012
Catalyst E	Al ₂ O ₃ -P/ZSM-5 (Catalyst A)	0.09% Ni	Aged & Decanted	14.9	34%	Not observed
Catalyst L	Al ₂ O ₃ -P/ZSM-5 (Catalyst A)	0.11% Pt	Aged & Decanted	13.5	17%	Not observed
Catalyst O	Al ₂ O ₃ -P/ZSM-5 (Catalyst A)	0.09% Pd	Aged & Decanted	13.6	18%	Not observed
Catalyst H	P/ZSM-5 (Catalyst H)	0	"As-is"	17.7	Base Case	-0.014
Catalyst I	P/ZSM-5 (Catalyst H)	0.08% Ni	Aged & Decanted	12.7	-28%	-0.170

X_{Tol} = Toluene conversion, mole%.

¹Relative activity increase of a catalyst is estimated by comparing toluene conversion obtained on the catalyst compared to that on base catalyst.

²Deactivation rate: Toluene conversion decline, mole% per 24 hour.

[0067] Table 7 also shows the comparison of toluene conversion and catalyst deactivation rate between Catalyst H (no metal) and Catalyst I (0.08 wt% Ni). Catalyst H is a self-bound P/ZSM-5 catalyst. Catalyst I was made by using Catalyst H and by using the same method as used for Catalyst E. Unexpectedly, Catalyst I did not show any increase in activity, but rather it showed a dramatic decrease in activity, and toluene conversion declined faster than for the base Catalyst H.

[0068] While the invention has been shown in only some of its forms, it should be apparent to those skilled in the art that it is not so limited, but is susceptible to various changes and modifications without departing from the scope of the invention. Accordingly, it is appropriate that the appended claims be construed broadly and in a manner consistent with the scope of the invention.

CLAIMS

We claim:

1. A method of forming a catalyst for use in aromatic alkylation, the method comprising:

treating a zeolite with a phosphorus-containing compound;

combining the phosphorus-treated zeolite with a binder material;

treating the bound phosphorus-treated zeolite with an aqueous solution of a hydrogenating metal compound by contacting the bound phosphorus-treated zeolite with the aqueous solution and separating the aqueous solution from the bound phosphorus-treated zeolite to form a hydrogenating-metal-containing zeolite catalyst.

2. The method of claim 1, wherein:

the zeolite is a ZSM-5 zeolite.

3. The method of claim 1, wherein:

the hydrogenating metal is Group VIIIA transition metal.

4. The method of claim 1, wherein:

the hydrogenating metal is selected from at least one of nickel, palladium and platinum.

5. The method of claim 1, wherein:

the hydrogenating-metal-containing zeolite is calcined at a temperature of from about 400 °C or higher.

6. The method of claim 1, wherein:

the hydrogenating metal is present in the catalyst an amount of from about 0.03% to about 5% by total weight of catalyst.

7. The method of claim 1, wherein:

the catalyst contains from about 0.01% to about 15% phosphorus by total weight of catalyst.

8. The method of claim 1, wherein:

the binder is an alumina binder.

9. The method of claim 1, wherein:

the binder is present in the catalyst in an amount of from about 1% to about 99% by total weight of the catalyst.

10. A hydrogenating-metal-containing zeolite catalyst for use in aromatic alkylation, the catalyst comprising in the following order:

- a) zeolite;
- b) phosphorus;
- c) binder; and
- d) a hydrogenating metal.

11. The catalyst of claim 10, wherein:

the catalyst is formed by treating a bound phosphorus-containing zeolite with an aqueous solution of a hydrogenating metal compound by contacting the bound phosphorus-containing zeolite with the aqueous solution and separating the aqueous solution from the bound phosphorus-containing zeolite to form the hydrogenating-metal-containing zeolite catalyst.

12. The catalyst of claim 10, wherein:

the zeolite is a ZSM-5 zeolite.

13. The catalyst of claim 10, wherein:

the hydrogenating metal is Group VIIIA transition metal.

14. The catalyst of claim 10, wherein:

the hydrogenating metal is selected from at least one of nickel, palladium and platinum.

15. The catalyst of claim 11, wherein:

the hydrogenating-metal-containing zeolite is calcined at a temperature of from about 400 °C or higher.

16. The catalyst of claim 10, wherein:

the hydrogenating metal is present in the catalyst an amount of from about 0.03% to about 5% by total weight of catalyst.

17. The catalyst of claim 10, wherein:

the catalyst contains from about 0.01% to about 15% phosphorus by total weight of catalyst.

18. The catalyst of claim 10, wherein:

the binder is an alumina binder.

19. The catalyst of claim 10, wherein:

the binder is present in the catalyst in an amount of from about 1% to about 99% by total weight of the catalyst.

20. A method of preparing an alkyl aromatic product comprising:

contacting a hydrogenating-metal-containing zeolite catalyst with an aromatic alkylation feed of an aromatic compound and an alkylating agent under reaction conditions suitable for aromatic alkylation, the hydrogenating-metal-containing zeolite catalyst comprised of a bound phosphorus-containing zeolite having in the following order: zeolite, phosphorus, a binder and a hydrogenating metal compound.

21. The method of claim 20, wherein:

a bound phosphorus-containing zeolite is treated with an aqueous solution of a hydrogenating metal compound by contacting the bound phosphorus-containing zeolite with the aqueous solution and separating the aqueous solution from the bound phosphorus-containing zeolite to form the hydrogenating-metal-containing zeolite catalyst.

22. The method of claim 20, wherein:

the hydrogenating-metal-containing zeolite is calcined at a temperature of from about 400 °C or higher prior to use in aromatic alkylation.

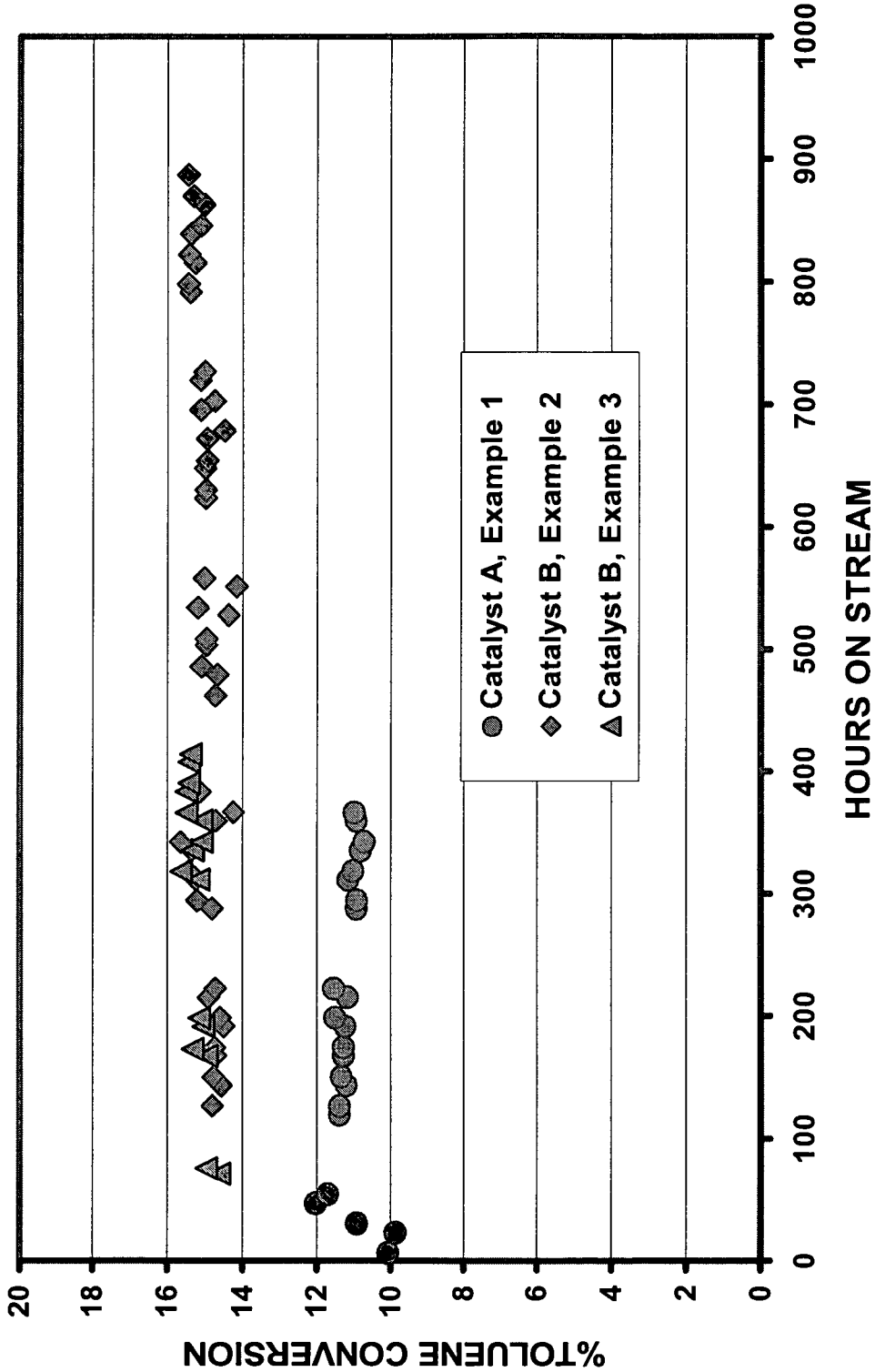


FIGURE 1

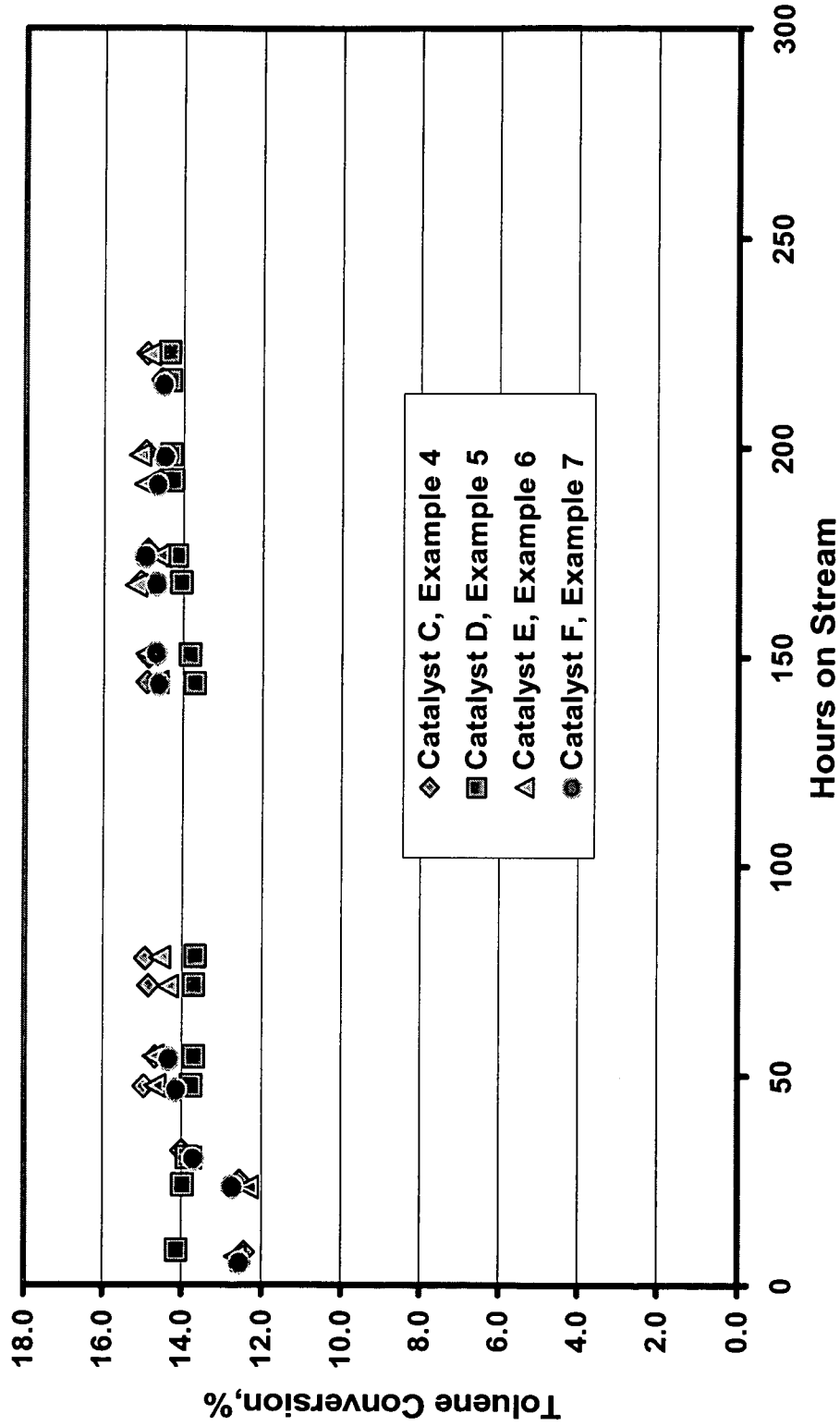


FIGURE 2

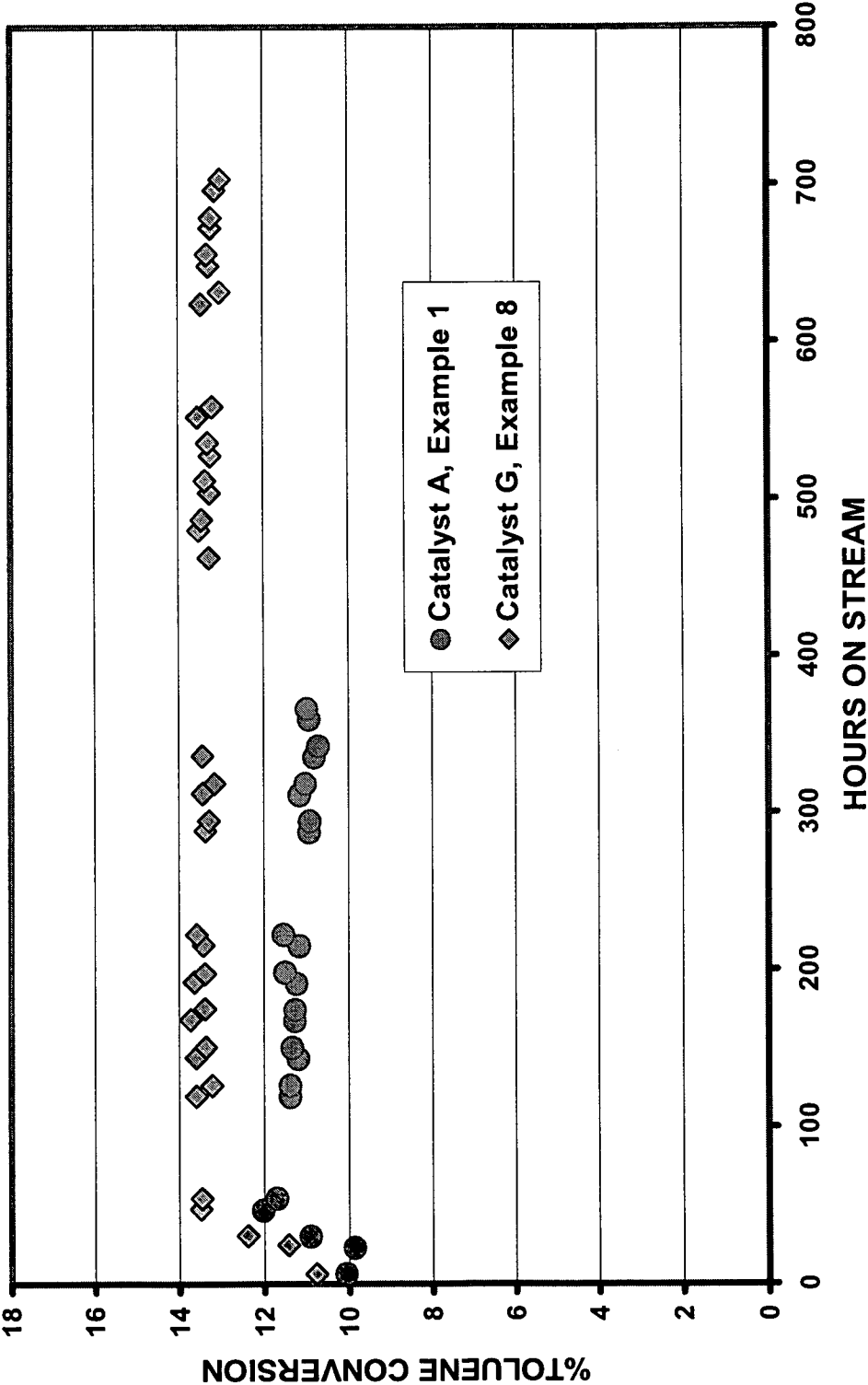


FIGURE 3

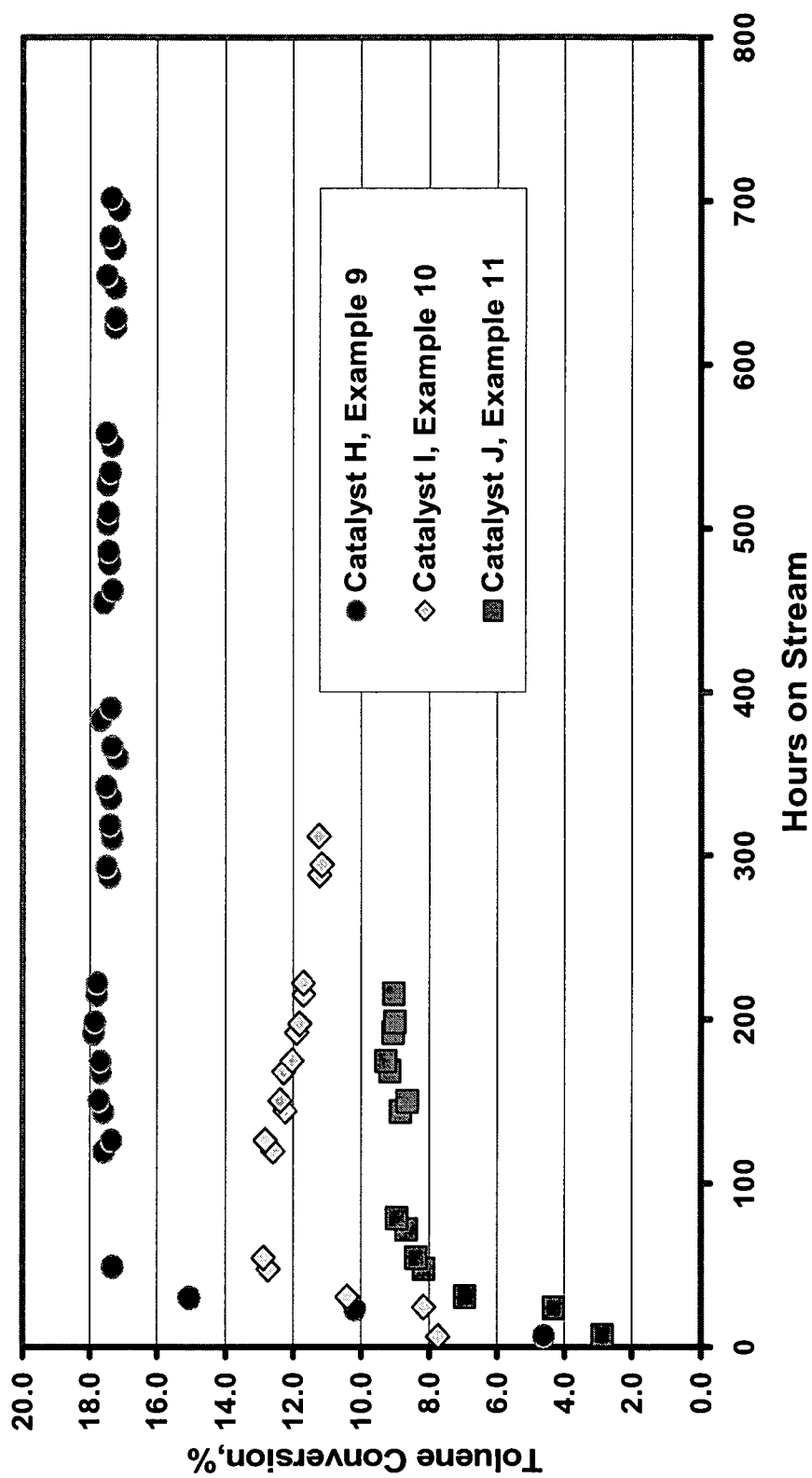


FIGURE 4

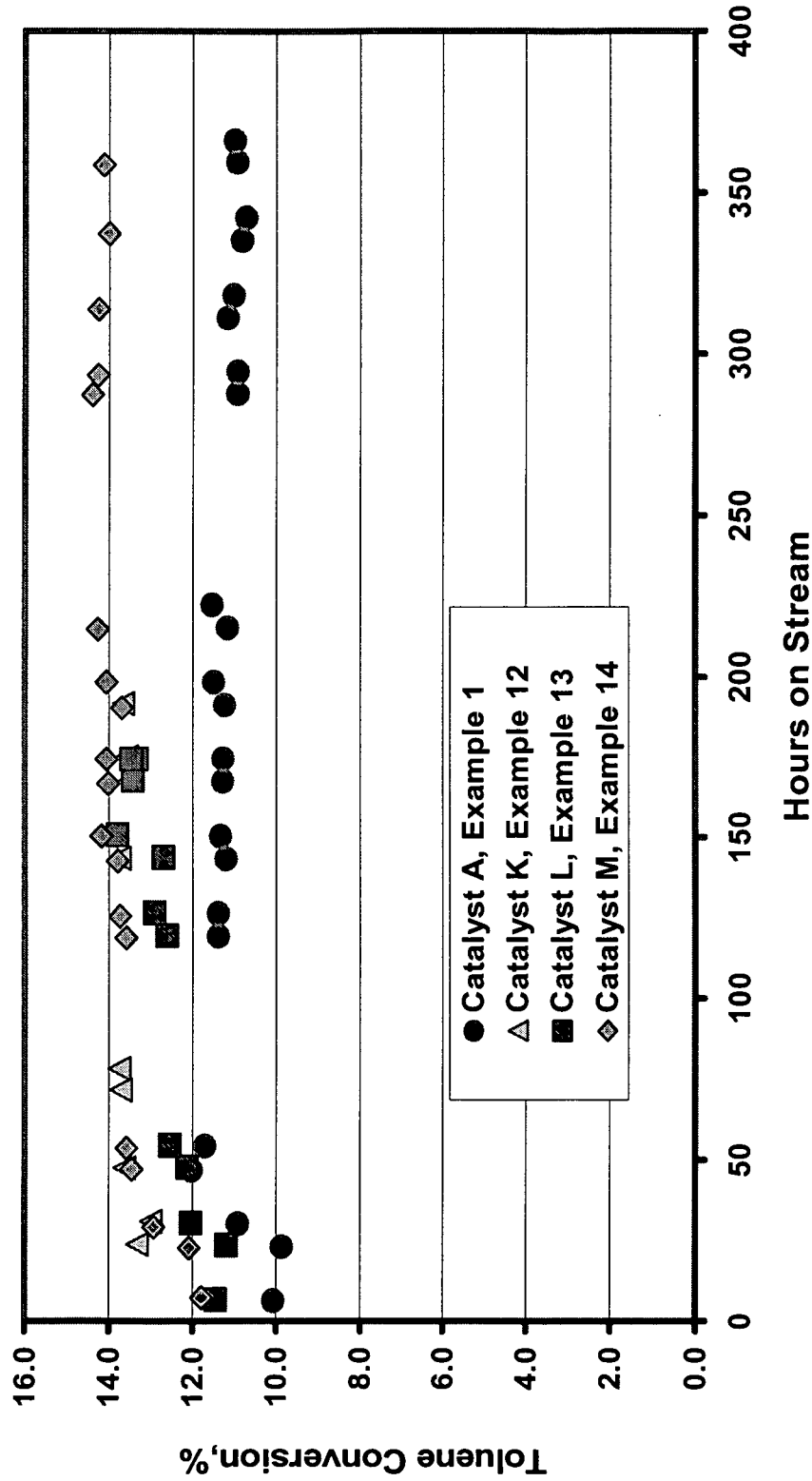


FIGURE 5

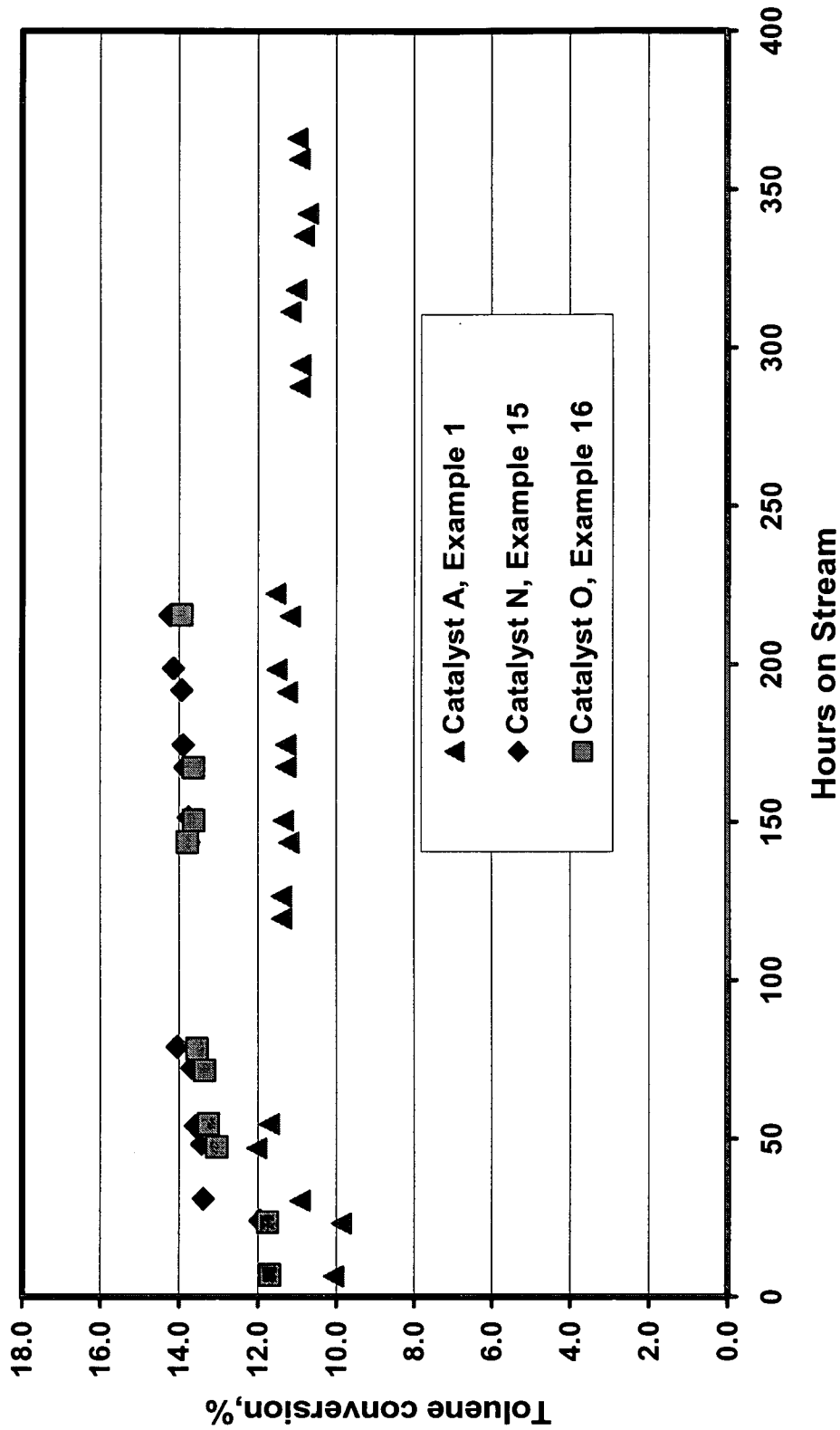


FIGURE 6

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 09/05613

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C07C 2/68 (2009.01)

USPC - 585/467

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)
USPC: 585/467,466;502/63,64,71.Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC: 585/467,466;502/63,64,71 and all USPC classes (text search - see terms below)Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWEST(USPT,PGPB,EPAB,JPAB);Google;Google Scholar
Search Terms: transition metal, Group VIIIA, Nickel, binder, calcine, phosphorus, metal, zeolite, molecular sieve, aromatic alkylation, toluene, toluol, methylbenzene, methanol, methylation, methyl alcohol, wood alcohol, hydrogenate, metal, treat, add, contact, evaporate,

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2008/0176736 A1 (GHOSH et al.) 24 July 2008 (24.07.2008), para [0018], [0020], [0021], [0023], [0024], [0028], [0032], [0033].	1-22
Y	US 2005/0143613 A1 (DAKKA et al.) 30 June 2005 (30.06.2005), para [0002], [0025], [0026].	1-22
Y	US 5,726,114 A (CHANG et al.) 10 March 1998 (10.03.1998), col 8, ln 13.	1-9, 11, 15, 21

☐ Further documents are listed in the continuation of Box C.

* 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 application or patent 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

01 December 2009 (01.12.2009)

Date of mailing of the international search report

11 DEC 2009

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450
Facsimile No. 571-273-3201

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774