ELSEVIER

Catalysis Today 38 (1997) 243–247

CATALYSIS TODAY

Zeolite based catalysts for linear alkylbenzene production: Dehydrogenation of long chain alkanes and benzene alkylation

P. Mériaudeau*, Y. Ben Taarit, A. Thangaraj, J.L.G. Almeida, C. Naccache

Institut de Recherches sur la Catalyse, CNRS, 2 avenue Albert Einstein, 69626 Villeurbanne, France

Abstract

Linear alkylbenzenes (LAB) obtained by alkylation of benzene with linear C_{10-14} olefins. In the present work we have investigated the dehydrogenation of long chain alkanes over Pt-based catalysts. For convenience *n*-octane dehydrogenation was used to probe the dehydrogenating properties of the catalysts. The catalysts for dehydrogenation of *n*-octane are constituted by Pt or Pt–In alloys supported on alumina, NaY, KL zeolites and on silicalite. The metal particles were characterized by STEM-EDX, H_2 adsorption, and IR of adsorbed CO. The main conclusions are: In Pt–In/silicalite system, very small metal particles, less than 1 nm, are formed that are localized in the silicalite pores and Pt is alloyed with In. These Pt–In particles show unexpected high dehydrogenating activity and very high stability against coking even in the absence of added hydrogen. The alkylation of benzene with 1-dodecene over H-form zeolites was investigated. The reaction temperature was in the range 373–473 K. Batch reactor was chosen for this study. The results indicate that dealuminated HY zeolites are apparently the most suitable catalysts. H-ZSM-5, H-ZSM-12 showed almost no activity for the production of LAB, due to the small size of the channels. The reaction was influenced considerably by diffusion. While H-mordenite also showed very low catalytic activity, dealuminated H-mordenite exhibited a significant activity and a very high selectivity for the production of 2-phenyldodecane which is the less bulky among the other phenyldodecane isomers. The mesoporosity generated within dealuminated mordenite is responsible for these observations.

Keywords: Zeolite; Alkylbenzene; Platimun-based catalyst; Olefin

1. Introduction

Sulphonated linear alkylbenzenes (LAB) are used in detergent manufacture. Currently, alkylbenzenes are manufactured by alkylation of benzene with C_{10}–C_{14} olefins in the presence of HF following the UOP process. Linear C_{10}–C_{14} olefins are produced by the dehydrogenation of linear C_{10}–C_{14} alkanes over Pt–Sn–Al_2O_3–Li catalysts. It is of great interest in relation to environment, industrial hazard and corrosion problems to replace HF (or $AlCl_3$) catalysts by non-corrosive solid acid catalysts.

A wide variety of heterogeneous catalysts has been investigated so far such as rare earth exchanged X and Y zeolites [1] silicotungstic acid supported on alumina [2], various ZSM zeolites [3,4], H-MCM-22 [5] and HY [6,7]. UOP-Petresa have recently announced a new process with a solid-acid catalyst. The aim of this study on benzene alkylation was to evaluate the effect of dealumination on the alkylation properties of HY and H-mordenite. H-ZSM-5 and H-ZSM-12 were also studied for comparison.

---

*Corresponding author. Fax: (33-3) 8244-5399.

PII S0920-5861(97)00073-4

It is well known that the best catalysts for the dehydrogenation of alkanes are generally based on Pt, preferentially supported on non-acidic support, Al_2O_3 neutralized by K^+ or Li^+, and that alloying Pt with tin or indium enhanced the stability of the Pt-catalysts towards deactivation by coke deposition. Furthermore it is well known that the increase of H_2 pressure improves considerably the resistance of the catalysts towards coke formation. In this work we have synthesized a new dehydrogenation catalyst by supporting Pt on an In-silicalite support, that shows almost no acidity. The dehydrogenation of *n*-octane was studied.

2. Experimental

The catalysts for *n*-octane dehydrogenation were prepared by supporting Pt on NaY commercial zeolite, KL from Union Carbide, γ-Al_2O_3, and In-silicalite or Sn-silicalite.

Indium silicalite and tin silicalite were synthesized in the laboratory following the procedure described in [8,9]. For the synthesis of In-silicalite tetraethylorthosilicate (TEOSi) was hydrolyzed with a solution of tetrapropylammonium hydroxide. To this solution a solution of $In(NO_3)_3$ (or $Sn(SO_4)_2$) was added. Crystallization occurred in an autoclave at 443 K for 4 days. A $[Pt(NH_3)_4]Cl_2$ solution was used to introduce platinum to zeolites by ion exchange, by impregnation to Al_2O_3. Indium was introduced into NaY, KL by ion exchange. Most of the catalysts contained 0.5 wt% Pt. The amount of In (or Sn) was varied between 0.8 and 2 wt%. In the present work we will discuss the results obtained for $Pt_{0.5}In_{1.6}$ silicalite, $Pt_{0.5}Sn_{0.5}$ silicalite, $Pt_{1.7}In_{1.4}NaY$, Pt_1In_1KL, and $Pt_{0.4}Sn_{0.4}In_{0.4}$–Al_2O_3 $Li_{0.3}$ (the subscript corresponds to the metal wt%).

Metal dispersion, particle size and composition were determined by H_2 adsorption, infrared of adsorbed CO, transmission electron microscopy, STEM and EDX.

The dehydrogenation of *n*-octane was studied in a continuous flow reactor at atmospheric pressure, $P_{H_2}/P_{nC_8}=0.5$, reaction temperature of 733 K. The space velocities for the different catalysts were such that one could obtain the same initial *n*-octane conversion for all samples, around 20%. Under these conditions, the products of *n*-octane reaction were *n*-octenes (60–70%), diolefins and aromatics (around 20–25%). Higher hydrocarbons were also formed.

The alkylation of benzene with 1-dodecene was carried in a batch reactor at 373–473 K. Analysis of the reaction was performed by collecting a very small fraction of the solution at different time. The procedure was described in [10]. The catalysts were HY zeolite, H-mordenite which have been dealuminated by steam treatment at a high temperature [10].

3. Results and discussion

3.1. Dehydrogenation of n-octane

The metal particle sizes determined by transmission electron microscopy were in the range 0.8–1.5 nm for all catalysts studied. These results were in good agreement with the metal dispersion measured by H_2 adsorption. Furthermore it was found that metal particles less than 0.8 nm size exist within the silicalite channels.

STEM-EDX analysis of Pt–In catalysts indicated that on each individual metal particles both Pt and In exist which should indicate that indeed Pt and In formed a bimetallic particle. However, careful analysis by STEM-EDX of the Pt–In-silicalite sample showed that within individual bimetallic particles the ratio Pt/In is much higher than that corresponding to the chemical analysis (see Table 1). By contrast when a large area of the sample is submitted to STEM-EDX analysis the Pt/In ratio is identical to the value derived from chemical analysis. It is concluded that only a part of In is alloyed with Pt with a large fraction remaining dispersed over the support.

The formation of Pt–In bimetallic particles was further supported by the infrared studies of adsorbed CO. In general the IR spectra of CO adsorbed on Pt-silicalite contained two bands, one at around 2050–2060 cm^{-1} attributed to linearly bonded CO on Pt sites

Table 1
STEM-EDX analysis of individual metal particles in Pt–In-silicalite

Number of analysis	Pt/In (wt%) STEM-EDX	Pt/In (wt%) Chemical analysis
22	49–14	4.5

and one at around 1890 cm^{-1} due to bridged CO. Pt–NaY as well as Pt–KL showed the same features. The IR band intensity of the bridged CO at 1890 cm^{-1} decreased considerably as the In content in the samples increased. These observations were indirect evidence of the formation of Pt–In bimetallic particles since it has been well established that upon alloying Pt with a second metal, the propensity of Pt to adsorb CO in a bridged form decreases considerably. The general conclusion derived from the characterization of the bimetallic particles present on silicalite, NaY and KL is that these particles are small in size, and are localized within the zeolite channels and/or cavities. Within each metal particle Pt is diluted with In (and/or Sn) atoms. More detailed characterization of these catalysts are given in Refs. [9–11].

The dehydrogenation of *n*-octane was studied at atmospheric pressure in a flow reactor at 733 K. The space velocity of the mixture $H_2/nC_8/N_2$ ($H_2/nC_8=0.5$) was different for each set of experiment in order to reach the same initial *n*-octane conversion over each catalyst. Fig. 1 shows the change in the activity of *n*-octane with time on stream for the different Pt catalysts listed above.

While there is an overall decrease in activity with time on stream in the case of Pt–In catalyst supported on NaY, KL or Al_2O_3–Li, it is clear that there is a considerable enhancement of the stability towards deactivation of Pt–In (or Pt–Sn) when the support is silicalite. Several factors explain the differences between the supports: (a) within the In-silicalite support In is atomically dispersed within the zeolite framework thus favouring upon H_2-reduction the formation of highly homogeneous Pt–In alloy resulting in lower hydrogenolysis of hydrocarbons; (b) Pt–In particles in silicalite are much smaller in size than Pt–In supported on other zeolites. Thus Pt–In-silicalite would have less propensity to generate carbon residues following hydrogenolysis; (c) within the channels of the silicalite support, the Pt–In particles are less sensitive to sintering and furthermore the shape selective properties of the silicalite due to the small size of its channels inhibits the formation of bulky carbonaceous residues responsible for the deactivation.

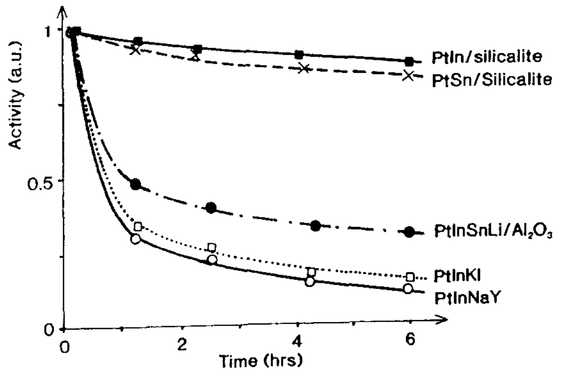

Fig. 1. Relative rate of nC_8 dehydrogenation as a function of time on stream $T=460^\circ C$, $P_{H_2}/P_{HC}=0.5$ atmospheric pressure, WHSV were adjusted to have identical initial conversion.

This work has demonstrated that there is a strong correlation between the catalyst microstructure and the stability and selectivity in alkanes dehydrogenation into alkenes. Pt when alloyed with indium or tin, and when stabilized within the narrow channels of non-acidic silicalite exhibits an unusual catalytic stability with time on stream. Much lower H_2 pressure may be used thus favouring the thermodynamics of the dehydrogenation reaction of alkanes.

3.2. Alkylation of benzene with 1-dodecene

As stated in Section 2 the alkylation reaction was studied in a batch reactor. The mole ratio benzene/dodecene=8 and the reaction temperature of 373 K were used as the standard experimental condition. Over HY zeolites, where the framework Al content was decreased through hydrothermal dealumination at high temperature, the main reactions occurring were the double bond migration in 1-dodecene molecule, thus generating almost the thermodynamic isomer distribution of dodecene 1, 2, 3, 4, 5 and 6, and the alkylation of benzene to produce all the phenyldodecane isomers.

The selectivity towards the production of phenyldodecanes (2, 3, 4, 5 and 6) was around 97%. Small amount of phenyldecane, didodecylbenzenes and alkyltetralines are also produced. It is probable that part of these bulky hydrocarbons remained trapped within the cavities of HY and that they are responsible for the deactivation of the zeolite with time on reaction.

The effect of dealumination of HY on the catalytic activity was studied. Samples were dealuminated at increasing level, the Al content in the framework

Table 2
Alkylation of benzene with 1-dodecene over H-ZSM-5, H-ZSM-12, H-mordenite (Si/Al=5.5)

Catalyst	Si/Al	Reaction temperature (K)	Isomerization of dodecene double bond	Rate of alkylation (mol/min per g)
H-ZSM-5	15	373	Yes	0
H-ZSM-12	80	373	Yes	0
H-Mordenite	5.5	373	Yes	0.001
HY	26	373	Yes	0.03

being decreased from 50 to 10 Al per unit cell. Simultaneously with the dealumination a mesoporosity (pore around 6 nm in size) was created. The effect of the dealumination was to increase not only the stability of the catalyst on reaction, but also to increase the diffusion of the molecules into and out of the pores. The efficiency of the zeolite was thus enhanced. Non-dealuminated HY deactivated very rapidly with time on reaction.

The effect of pore size and secondary mesoporosity on the rate of benzene alkylation with 1-dodecene was further investigated. H-ZSM-5 (pore 0.56×0.53 nm) H-ZSM-12 (monodimensional channels of 0.62 nm) H-mordenite (monodimensional channel of 0.7 nm) were used as catalysts.

In Table 2 are listed the results of the alkylation reaction. This table indicates that although the acidity of the various zeolites is sufficient to catalyse the migration of the double bond in 1-dodecene, the alkylation reaction does not occur on H-ZSM-5, H-ZSM-12, H-mordenite at 373 K. However it was found that by increasing the reaction temperature up to 453 K both H-ZSM-12 and H-mordenite showed a relatively small activity. Over these catalysts the 2-phenyldodecane (which is less bulky relative to other phenyldodecane isomers 3, 4, 5, 6) selectivity was higher than 90%, while on HY the selectivity towards 2-phenyldodecane was never larger than 20–25%. The low performance of H-ZSM-5, H–ZSM-12 and H-mordenite in the alkylation of benzene with 1-dodecene, despite the presence of acid sites, must be attributed to the very low diffusion of reactants and more to the lack of large enough void space allowing the formation of the bulky phenyldodecane intermediates. By increasing the reaction temperature one could suggest that the diffusion of the reactants increases such that although the reaction rate remains diffusion control, 2-phenyldodecane could diffuse out of the channels. The absence of 3-, 4-, 5- and 6-phenyl dodecanes clearly indicates that shape selective reaction by intermediate shape selectivity is prevailing. These conclusions were reinforced by the study of dealuminated H-mordenite. Dealuminated H-mordenite presents a mesoporosity and simultaneously the activity of these samples is considerably enhanced. Within the mesopore system existing in dealuminated mordenite, the diffusion of the molecules is considerably enhanced. The more open channel system in dealuminated-mordenite allows a much higher rate of reaction.

The high open pore system of HY appears more suitable for the production of LAB, since these bulky molecules must diffuse rapidly out of the pores: the rapid diffusion of alkylbenzenes, such as phenyldodecanes, not only results in a higher rate of reaction but also limits secondary reactions such as multiple alkylation event, cyclization of the lateral chains to produce indane and alkylindanes, etc.

The relation existing between the acidity and the rate of the benzene alkylation was studied. The effect of the total number of acid sites present in HY on the rate of alkylation was studied by using a series of dealuminated HY samples.

Fig. 2 shows that there exists almost a linear relation between the rate of benzene alkylation with 1-dodecene and the number of Al atoms in the framework, that is, with the number of acid sites. It is clear that the most suitable HY samples for this reaction will be those showing the greatest number of acid sites with the most open mesoporosity.

The effect of acid strength on the rate of alkylation was studied by using a series of H-NaY zeolites for which the degree of ion exchange of Na^+ with H^+ was increased. It is well accepted that less is the sodium content higher is the proton acid strength. Thus decreasing the sodium content in HY increases not

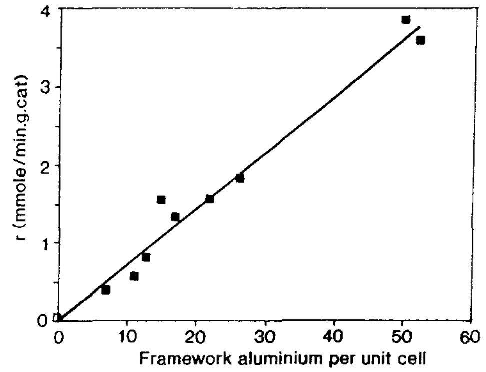

Fig. 2. Effect of framework aluminium content on the alkylation over dealuminated HY.

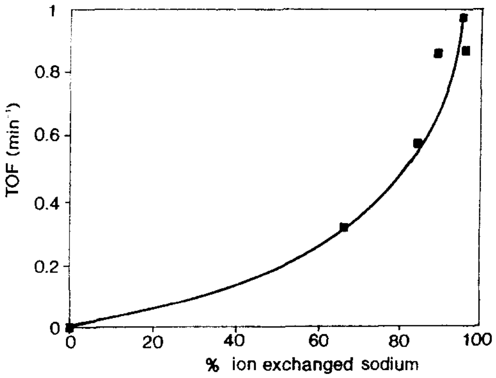

Fig. 3. Effect of the sodium ion-exchange level of HNaY on the alkylation reaction TOF.

only the number of acid sites but also the acid strength. Fig. 3 shows the turnover frequency (TOF) for the alkylation of benzene with 1-dodecene versus the ion exchange level. It is clear that the efficiency of each individual acid site increased significantly as the Na^+ content decreased.

In conclusion, medium pore zeolites such as ZSM-5, as well monodimensional pore system zeolites such as ZSM-12, mordenite, exhibit low activity in the alkylation of benzene with long chain linear olefins. For this reaction tridimensional large pore zeolites such as HY should be preferred. Over these later catalysts the selectivity towards monoalkylbenzenes is higher than 95%. Small amount of residual sodium has a substantial detrimental effect on the performances of the solid. Furthermore in order to avoid rapid deactivation by residual bulky hydrocarbons, which poison the acid sites and also block the access of the pores, and to increase the rate of diffusion of reactants and products, it is recommended to create within the micro-structure of the HY a mesoporosity system. Apparently hydrothermal dealumination operates most efficiently.

References

[1] P.B. Venuto, A.L. Hamilton, P.S. Landis and J.J. Wise, J. Catal., 5 (1996) 81.

[2] R.T. Sebulsky and A.M. Henke, Ind. Eng. Chem. Process Des. Dev., 10 (1971) 272.

[3] L.B. Young, N.J. Skillman, US Patent 4301317 (1981).

[4] H. Ming-Yuan, L. Zhonghui and M. Enze, Cataly. Today, 2 (1988) 321.

[5] Q.N. Le, D.O. Marler, J.P. Mc Williams, M.K. Rubin, J. Schim, S.S. Wong, US Patent 4962256 (1990).

[6] S. Sivasanker and A. Thangaraj, J. Catal., 138 (1992) 386.

[7] S. Sivasanker, A. Thangaraj, R.A. Abulla, P. Ratnasamy, in: Guczi et al. (Eds.), Proceedings of the International Congress on Catalysis, New Frontiers in Catalysis, vol. 75, Elsevier, Amsterdam, 1992, p. 397.

[8] P. Mériaudeau, A. Thangaraj, S. Narayanan and C. Naccache, J. Catal., 148 (1994) 617.

[9] P. Mériaudeau, G. Sapaly, A. Thangaraj, C. Naccache, S. Narayanan, Indian Patent 1433 (December 1993).

[10] J.L.G. de Almedia, M. Dufaux, Y. Ben Taarit and C. Naccache, Appl. Catal. A , 114 (1994) 141.

[11] P. Mériaudeau, C. Naccache, A. Thangaraj, C.L. Bianchi, R. Carli, V. Vishvanathan and S. Narayanan, J. Catal., 154 (1995) 345.