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Hydroisomerization of a hydrocarbon feed containing *n-hexane* on Pt/H-Beta and Pt/H-Mordenite catalysts

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Abstract

Bifunctional Pt/H-Beta and Pt/H-Mordenite catalysts were prepared by using incipient wetness impregnation method to obtain a 0.5 wt% metal load and applied to the Isomerization of n-hexane. Commercial Pt/H-Beta gave rise to a higher yield of high octane Dimethylbutanes (DMB) than the commercial Pt/H-Mordenite. To explain this result, both the dispersion and distribution of Pt clusters in the zeolite channels were investigated. The acidity and distribution of acid sites were examined by using ammonia and pyridine as probe molecules. Pt/H-Beta was found to be a potential catalyst for the Isomerization of n-hexane because Pt clusters could be well dispersed to give proper balance between metallic centers and acid sites in H-Beta zeolite although its acidity was low as compared to H-Mordenite.

Keywords: Metal-supported catalysts, Zeolite, Isomerization, n-hexane, Acidity, ammonia, pyridine

Introduction

The demand for branched alkanes increases in the reformulated gasoline pools due to the environmental regulation such as elimination of lead alkyl additives and limitation in the content of olefins, benzene and total aromatics. The Pt/chlorinated-alumina has been commercially used in the industrial process for the isomerization of n-paraffins [1]. Pt/H-MOR has also been considered as a new generation of commercial catalyst for C_5/C_6 paraffin isomerization [2]. More recently, some authors have reported that zeolite beta and mazzite would be potential acid catalysts for Hydroisomerization of n-alkanes [3]. However, the characteristics features of and comparative studies between Pt/H-MOR and Pt/H-beta for alkane isomerization are not clearly available. The activity of bifunctional Pt/zeolite catalyst is strongly influenced not only by the number of acidic and metallic centers but also by the distribution of these clusters as well as the metal dispersion in the zeolite depends on the calcination and reduction conditions and thereby exercises influence over the activity for the isomerization of *n*-alkanes [4].

The purpose of this study is to examine the changes in the distribution and dispersion of metal clusters in the zeolite channels with the pretreatment conditions and their effects in the isomerization of *n*-hexane. The acidic properties of H-MOR and H-beta are to be investigated by using ammonia and pyridine as probe molecules. Finally, the difference in activity between Pt/H-MOR and Pt/H-beta will be discussed in detail.

Materials and Methods

Experimental Section

Preparation of catalysts

Zeolite Beta and Mordenite were purchased from Zeolyst Int. (refs. CP914, CBV8014, CBV21A, CBV90A, CP814E, CP811E-75 and CBV760). All supports were calcined at 580^0C prior to impregnation. Platinum was deposited onto the zeolites by impregnation to incipient wetness; a volume of 5.1ml of a 5 X 10^{-3}M $Pt(NH_3)_4(NO_3)_2$ solution per gram of zeolite was used to obtain a metal load of 0.5 wt% on the support. Platinum loaded catalysts were dried at 110^0C overnight and then heated at a rate of 0.5^0C/min in O_2 flow (11/min g cat) up to various calcination temperatures T_c (200, 300, 350, 400 and 500^0C). The catalysts were maintained at each of these temperatures for 2 hours and allowed to cool down to the room temperature in He flow. Reduction was then performed in H_2 flow (200cm^3/min g cat) by raising the temperature at a rate of 2^0C/min to 500^0C and the temperature was held at 500^0C for 1 hour. Physicochemical properties of the catalysts examined in this study are summarized in Table 1.

Catalyst Characterization:

For Temperature Programmed Desorption (TPD) analysis, the bed of H-form zeolite (0.1g) was heated at 500^0C in He flow into the bed after cooling the bed to 100^0C or 200^0C respectively. The TPD was started by increasing the temperature at a rate of 15^0C/min. Temperature Programmed Reduction (TPR) experiment was conducted for the Pt/H-MOR and Pt/H-beta catalysts calcined up to various temperatures. After calcination, the catalysts were cooled down to room temperature in N_2 flow. A continuous flow of H_2 (6 vol%) in N_2 carrier was directed over the catalysts and the temperature was increased from the room temperature to 715^0C at a rate of 10^0C/min.

Reaction Experiment:

The reaction experiment was conducted in a fixed-bed downflow reactor with H_2/*n-hexane* molar ratio of 6.0 under the atmospheric pressure. *N-hexane* (purity >99.5%) was fed to the reactor in H_2 flow by a microfeeder. The product was analyzed by on-line GC with FID and the analysis column was made of stainless-steel tube packed with Chemi-pack C_{18}. The hydrogenation of benzene was also conducted at 100^0C with H_2/benzene molar ratio of 9.8 and WHSV = 29.3h^{-1} under the atmospheric pressure.

Results and Discussion

TPD using ammonia and pyridine

The result of TPD for both H-beta and H-MOR are summarized in Table 1. Intense low temperature peak appeared for both zeolites due to the weakly adsorbed ammonia on silanol groups. The area and the position of high-temperature desorption peak, related to desorption of ammonia from strong acid sites, turned out to be much higher over H-MOR than over H-beta. This implies that the acidity of H-MOR is much stronger than that of H-beta [5].

Table 1 – Physicochemical properties and acidic properties of catalysts used in this study

Catalyst	**Si/Al**	**BET results**		**NH_3-TPD (mmol/g cat)**		**Pyridine-TPD (µmol/g cat)**	
		Sg (m^2/g cat)	**Vp Cc/g cat)**	**LT-peak[a] (T_m, ^0C)**	**HT-Peak[b] (T_m, ^0C)**	**LT-Peak[C]**	**HT-Peak[d]**
H-MOR	6.5	501	0.209	0.63 (230)	0.48 (550)	12.72	10.50
H-beta	15.4	698	0.234	0.44 (225)	0.29 (375)	19.15	33.03

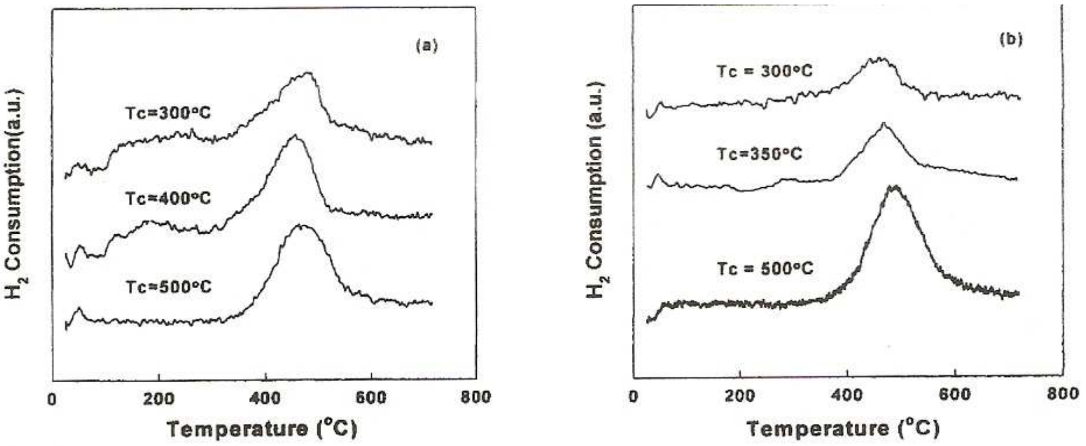
a – Ammonia desorbed at 100~325^0C; b – Ammonia desorbed above 325^0C; c – Pyridine desorbed at 200~400^0C; d – Pyridine desorbed above 400^0C

While ammonia (Kinetic diameter approx. 3.57^0A) can have access to almost all the acid sites in the microporous zeolites, pyridine with kinetic diameter of about 5.85^0A may not approach to the acid sites situated in relatively small pores. The results of TPD using pyridine are also given in Table 1. The acidity determined by pyridine TPD conflicted with the “total acidity” probed by TPD suing ammonia. As complied in Table 1, the amount of desorbed pyridine was much larger over H-beta. Based on these results, one may deduce that there exist more acid sites, which could serve as adsorption sites for relatively larger molecules such as mono- and di- branched isoalkanes in H-beta compared with H-MOR [6].

TPR of catalysts

Presented in Figure 1 are the TPR profiles obtained from Pt/H-MOR and Pt/H-beta calcined at various temperatures. The two major peaks at low and high temperatures are designated as α and β peaks, respectively. We notice from Figure 1 that while the H_2 consumption remained nearly constant for Pt/H-MOR irrespective of T_c it increased with T_c for Pt/H-beta. The large amount of H_2 consumption in Pt/H-MOR compared with Pt/H-beta calcined at temperatures below 500^0C indicates that there were some PtO_2 species formed by autoreduction of $Pt(NH_3)_4^{2+}$ ions during oxidative deammination. For Pt/H-beta calcined at 500^0C, the H_2 consumption was as high as that for Pt/H-MOR and this indicates the existence of Pt^{4+} species.

Fig. 1: TRP Profiles from (a) Pt/H-MOR and (b) Pt/H-beta, respectively calcined at various temperatures



In contrast to the case of Pt/H-MOR, the α peaks were not detected from Pt/H-beta. Preferential sites for extra framework charge-balancing cations in H-MOR are the center of 8-MR and the wall of the main channel [7, 8]. After the ion-exchange, however, $Pt(NH_3)_4^{2+}$ cations were presumably located in the main channel rather than in the side pocket of 8-MR because the cations would not be allowed to diffuse into the side pockets due to their size. Once the cations were completely decomposed to Pt^{2+} ions, the ions would be located both in the main channels and in the side pockets. Accordingly, the two TPR peaks above 100^0C could be attributed to the reduction of Pt^{2+} ions located in the main channels of 12-MR and those at some hidden sites including the sites in the side pockets. The area of α peak decreased with T_c and α peak disappeared when Pt/H-MOR was calcined at 500^0C. In addition, this temperature for complete reduction shifted to the higher temperature range. These results suggested that as T_c was increased, the Pt^{2+} ions initially located in the wall of the main channel might have slowly migrated into the side pockets in which Pt^{2+} ions could form more stable coordination with the zeolite.

Table 2 – Steady State product distribution from isomerization of *n*-hexane over Pt/H-MOR and Pt/H-beta catalysts

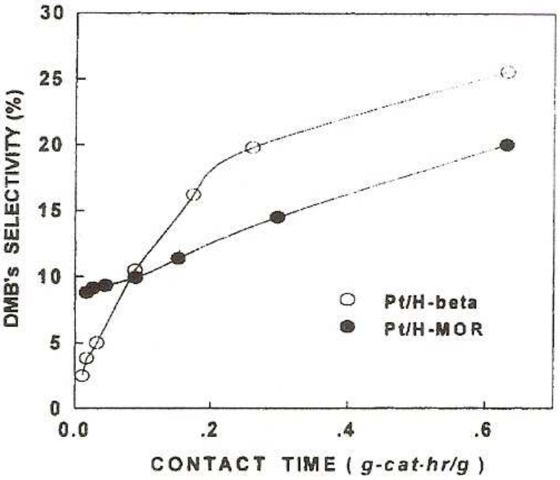
Catalysts	$T(^0C)$	**Conversion (%)**	**Product composition (wt %)**				**Σ*i*-C$_6$**	***i*-C$_6$ Selectivity (%)**
			C$_1$-C$_5$	**2-MP[a]**	**3-MP[b]**	**ΣDMB[c]**		
Pt/H-MOR	270	70.7	1.2	33.8	21.8	13.9	69.5	98.3
	280	74.3	4.7	33.2	22.6	15.0	70.8	95.3
Pt/H-beta	270	78.4	1.2	34.8	22.6	19.7	77.1	98.4
	280	82.0	3.2	33.3	21.7	23.7	78.7	97.1

Reaction Conditions: H_2/n-hexane=6.0, WHSV=1.58h^{-1}, Total pressure=1 atm.
a – 2 – Methylpentane; b – 3 – Methylpentane; c – 2,3-Dimethylbutane + 2,2-dimetnylbutane

Comparison of the catalytic activity between Pt/H-MOR and Pt/H-beta

The composition of reaction products over Pt/H-MOR and Pt/H-beta are given in Table 2. For both catalysts, the highest yield of *i-hexane* was obtained at 280^{0}C. The catalytic activity of Pt/H-beta was higher than that of Pt/H-MOR despite the higher acidity of the latter catalyst. It is to be noticed that the difference in activity between the two catalysts resulted in the difference in the yield of Dimethyl Butanes (DMBs). The yield of methyl pentanes (MPs) was nearly the same over both catalysts but the yield of DMBs was much higher over Pt/H-beta than over Pt/H-MOR. The selectivity to DMBs at 270^{0}C is plotted against the contact time in Figure 2. At low contact time (or conversion), the selectivity to DMBs over Pt/H-MOR was higher than that over Pt/H-beta. As the contact time increases, however, the selectivity was reversed between the two catalysts. The reversion of DMBs selectivity may be attributed to the combined effect of acidity, channel structure including pore size and dispersion as well as distribution of metallic centers.

Fig. 2: Selectivity of DMBs as a function of the contact time over Pt/H-beta and Pt/H-MOR catalysts at 270^{0}C (H_2/*n*-Hexane=6.0)



At low contact time, the rate of formation of DMBs from MPs was higher over Pt/H-MOR because the acidity of H-MOR was much higher than that of H-beta. At high contact time, the residence time of carbenium ions on acid sites would become much larger and thus the structural effect and metal function in zeolite channels appear to play important roles in the formation of DMBs.

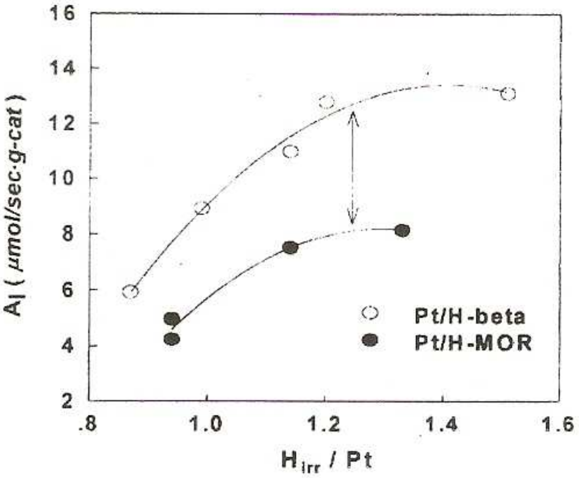
Effect of thermal activation

The Pt/H-MOR and Pt/H-beta catalysts were pretreated at various calcination and reduction temperatures to examine the effect of thermal activation of the isomerization of *n*-hexane. The catalytic activity for the isomerization of *n*-hexane is presented in Table 2. The highest activity was obtained for both catalysts calcined at 300-350^{0}C and subsequently reduced at 500^{0}C. Then T_c was increased, the activity decreased rapidly.

If the acidities of both Pt/H-MOR and Pt/H-beta are unaffected by the thermal activation conditions adopted in this study, the activity variation may be ascribed to the change in metallic centers. The activities of Pt/H-MOR and Pt/H-beta are plotted against Hirr/Pt value in Figure 3.

When the Hirr/Pt value was low, the activity increased almost linearly with Hirr/Pt and then approached to a limiting value as Hirr/Pt increased. The ratios of metal sites to strong acid sites in the range of Hirr/Pt showing constant activity in Figure 3 corresponds to 0.4 and 0.7 for Pt/H-MOR and Pt/H-beta respectively. These values were higher then the ratio that was suggested as the critical ratio by Zholobenko et al [8] for the optimum performance with respect to *n*-heptane isomerization.

Fig. 3: Activity (A_1) for the isomerization of *n*-hexane as a function of H_{irr}/Pt over Pt/H-MOR and Pt/H-beta



For identical value of Hirr/Pt/H-beta, the activity of Pt/H-beta was higher than that of Pt/H-MOR and the difference in activity became larger as Hirr/Pt increased. The isomerization of *n*-hexane is believed to take place via a bifunctional mechanism [9], involving both acid and metal sites. When metal loading is low, the activity increases proportionally to the hydrogenation function. If the metal component is present in sufficient excess to establish equilibrium between paraffin and associated olefin the activity is then governed by the acid function. The equilibrium was found to be established by loading 0.2-0.5 wt% of Pt in the study of Leu et al [3] and Degnan et al [9]. This was also confirmed by our experimental results. For identical Hirr/Pt value, the activity of Pt/H-beta was higher then that of Pt/H-MOR and difference in the activity became larger as H_{irr}/Pt increased. If the number of metal sites is identical, the distribution of Pt clusters in zeolite channels would be responsible for the difference in activity.

To compare the hydrogenation activity between Pt/H-MOR and Pt/H-beta, the hydrogenation of benzene was conducted. If most of the Pt clusters were located on the outer surface of the zeolite crystallites, Pt/H-MOR and Pt/H-beta catalysts would not have shown such a large difference in the hydrogenation activity. The hydrogenation activity of Pt/H-beta however, was extremely high in comparison to that of Pt/H-MOR when the Pt dispersion was about the same for both catalysts as shown in Table 2. Therefore, the large difference in hydrogenation activity between the two catalysts might be attributed to the difference in the accessibility of benzene to the Pt clusters in the zeolite channels.

According to the TPR results, some Pt clusters remained isolated in the side pockets of H-MOR and these metallic centers may not serve as dehydrogenation/hydrogenation sites during the isomerization of *n*-hexane. In such a case, the metal/acid ratio in the main channel of H-MOR will decrease so the selectivity to DMBs should be low at high conversion level over Pt/H-MOR as shown in Figure 2.

In addition to the detrimental loss of metallic centers, Mordenite has one-dimensional pore structure with side pockets at the wall of main channels, so if the platinum clusters in the main channel grow in size to fit the pore size of H-MOR during the reduction step, many of acid sites as well as platinum clusters located in the interior to the pore-plugging large clusters near the pore mouth would become inaccessible to the reactant and reaction intermediates. On the other hand, zeolite beta consists of intergrowth of linear channels (5.7 X 7.5 ^{0}A) of 12-MR and tortuous channels (6.5 X 5.6^{0}A) with channel intersections. Therefore, even if one of the channels are blocked by large particles (the linear channel might be blocked first), reactant and reaction intermediates might have access to some of metal sites through the other channels. In conclusion, there are much more platinum sites that are accessible to benzene in Pt/H-beta and the diffusion of benzene to metal sites in Pt/H-beta would be much easier than in Pt/H-MOR.

Conclusion

The bifunctional Pt/H-MOR and Pt/H-beta were prepared and their characteristics for the isomerization of *n*-hexane were elucidated. Both the catalytic activity and the selectivity to high octane DMBs were higher over Pt/H-beta than over the commercial Pt/H-MOR. However, the selectivity was found dependent upon the conversion of *n*-hexane. The catalyst calcined at 350^{0}C and subsequently reduced at 500^{0}C gave rise to the highest metal dispersion and the best activity. Although the “total acidity” probed by ammonia was higher over H-MOR, the “effective acidity” probed by pyridine was much higher over H-beta. For both Pt/H-MOR and Pt/H-beta, Pt clusters were found not only highly dispersed but also well distributed within the zeolite channels. For Pt/H-MOR however, some of Pt clusters were isolated in the side pockets of 8-MR and these metallic centers increased in population with the calcination temperatures. In addition, pore blockage of H-MOR channels by large Pt clusters could have made come of the Pt sites inaccessible to reactant and reaction intermediates. Due to these effects, the hydrogenation activity of Pt/H-beta was observed much higher than that of Pt/H-MOR when the dispersion was identical for both catalysts.

In conclusion the yield of DMBs over Pt/H-beta was higher than that over Pt/H-MOR because there were more acid sites accessible to bulky reaction intermediates such as methylpentanes and dimethylbutenes and Pt clusters were well dispersed in such way that the metallic centers might be balanced with acid sites in Pt/H-beta.

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