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GEOMETRIC AND PROMOTING EFFECTS OF METHYLCYCLOPENTANE CONVERSION OVER ALKALINE Pt/L ZEOLITES

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The hydrogenolysis of methylcyclopentane (MCP) has been used as a test reaction to analyze geometric and promoting effects in Pt catalysts supported on alkaline L zeolites. It has been observed that the production of 3-methylpentane (3MP) over these catalysts is significantly higher than over other Pt catalysts. Based on the micro-geometry of the system, we propose that collimating (geometric) effects play an important role in hydrocarbon reactions on these catalysts. On the other hand, the increased activity exhibited by the KL zeolite-supported catalysts relative to SiO_2-supported catalysts might indicate that promoting effects are also operative.

1. Introduction

The remarkably high selectivity observed over Pt/L zeolite catalysts for aromatization of n-hexane to benzene has attracted considerable attention [1–4]. In addition to the commercial interest that these systems have certainly induced [5,6], a stimulating scientific discussion has arised concerning the nature of their special properties. Two main approaches have been used to explain their unique selectivity.

The first one takes into account that, being non-acidic, these Pt catalysts must be mono-functional [1]. Therefore, in principle, any modification of the catalytic properties could be ascribed to alterations of the metal. Those who support this approach believe that the small Pt crystallites inside the cages of the L zeolite can be promoted by an interaction with the alkaline zeolite. This view was reinforced by a clear trend in catalytic activity reported by Besoukhanova et al. [2] over a Pt/L zeolite series exchanged with Li, Na, Rb or Cs. It was observed that when going from Li-exchanged zeolites to Cs-exchanged zeolites, the selectivity towards benzene formation increased from 42 to 85% while the overall conversion increased by a factor of 3. These authors also showed that a consistent trend could be obtained when the i.r. vibrational frequencies of adsorbed CO were compared on this series. A clear decrease in C-O frequency, consistent with an increased back-donation and an excess of electrons in the metal, was observed as the basicity of the zeolite was increased.

The second view, which could be considered of a geometric nature, ascribes the unique behavior of these systems to a special ability of the zeolite to either:

a) collimate the flux of n-hexane molecules [7], or

b) confine them in the cage through a non-binding interaction and pre-organize them as a pseudo-cyclic molecule [8,9].

Larsen and Haller [10], with whom we are currently carrying out a cooperative research program, have recently used the competitive hydrogenation of benzene and toluene as a probe for electronic alterations of these Pt catalysts. As a complementary study, we have chosen the hydrogenolysis of MCP, which in turn is generally believed to be very sensitive to the structural (geometric) characteristics of the catalysts. We attempt to demonstrate that, on these catalysts, both, promoting and collimating (geometric) effects play an important role in hydrocarbon reactions.

2. Experimental

We have studied two Pt/KL zeolite catalysts and a Pt/SiO_2 catalyst, provided by Prof. G.L. Haller. The Pt/KL catalysts were prepared by contacting the KL zeolite, 100–150 mesh (from Tosoh Corp., Japan) at room temperature during 24 h with solutions of $Pt(NH_3)_4(NO_3)_2$. Subsequently, the catalysts were washed, dried in air at 383 K, calcined in O_2 at 623 K for 5 h, flushed with He and reduced in H_2 at 623 K. The resulting solids were cation exchanged for 60 h at room temperature with KNO_3 solution. Using this exchange sequence, we eliminate any possible acid sites, which could have been generated during the reduction of Pt cations. The Pt/SiO_2 catalyst was prepared by impregnating SiO_2, CabOSil, 200 m^2/g from Cabot Corp., with a $PtCl_6H_2$ solution. Then, it was calcined at 463 K and reduced in H_2 at 723 K. Table 1 summarizes the main characteristics of the catalysts investigated.

Table 1

Catalyst	Pt (% wt)	Support	H/Pt	Exchanged cation	TON $(sec)^{-1}$ at 513 K
Pt/KL	1.03	L zeolite	1.0	K	2.50
Pt/KL	0.15	L zeolite	1.0	K	0.50
Pt/SiO_2	1.95	Cab-O-Sil	0.5	–	0.15

The catalysts were characterized by H_2 chemisorption and electron microscopy. The TEM observations were conducted in a JEOL TEM 100CX after reduction at 623 K and subsequent exposure to air. The hydrogenolysis of MCP was used as a test reaction. The activity measurements were performed in a micro-catalytic pulse reactor. Prior to reaction, all the samples were reduced in situ at 623 K. In each run, a gaseous 400 μl pulse of 6.8% MCP in hydrogen was injected into the H_2 stream which acted as a carrier. The products were analyzed by gas chromatography, using a 30% DC200/500 on Chromosorb P A/W 60–80 column from Supelco. The only products obtained under our reaction conditions were 2MP, 3MP and n-hexane. When the K-exchange was not performed after the reduction of Pt cations and the catalyst retained some acidity a significant fraction of C_1–C_5 was obtained.

3. Results

The TEM studies indicated that the SiO_2-supported catalyst exhibited a small, but clearly detectable fraction of particles larger than 100 Å. By contrast, only a few of such large particles were observed on the 1.03% Pt/KL and none on the 0.15% Pt/KL catalyst. On these catalysts, particles smaller than 30 Å were clearly seen. These observations would suggest that, in these catalysts, most of the metal is inside the zeolite.

In table 1 catalytic activities of the three catalysts investigated are compared. The TON for the hydrogenolysis of MCP at 533 K are based on H/M values. A clear increase in activity is observed for the Pt/KL catalysts in comparison with the Pt/SiO_2 catalyst. This increase is particularly pronounced for the 1.03% Pt catalyst.

Not only the level of activity, but also the product distribution markedly change over the Pt/KL catalysts relative to Pt/SiO_2. As illustrated in figs. 1a and 1b, a significant increase in the percentage of 3MP is observed over the two Pt/KL catalysts. It is known that the product distribution may vary with reaction temperature and conversion level. Therefore, we have made the comparison at both, constant conversion (fig. 1a) and constant temperature (fig. 1b), observing the same trend in each case.

4. Discussion

The hydrogenolysis of MCP over Pt catalysts has been widely investigated as a model reaction for mechanistic studies. Its product distribution has been shown to strongly depend on structural characteristics of the metal catalysts, e.g. particle size, exposed crystal plane, nature of the support, presence of surface contaminants, etc. In consequence, it has also been widely used as a test reaction for

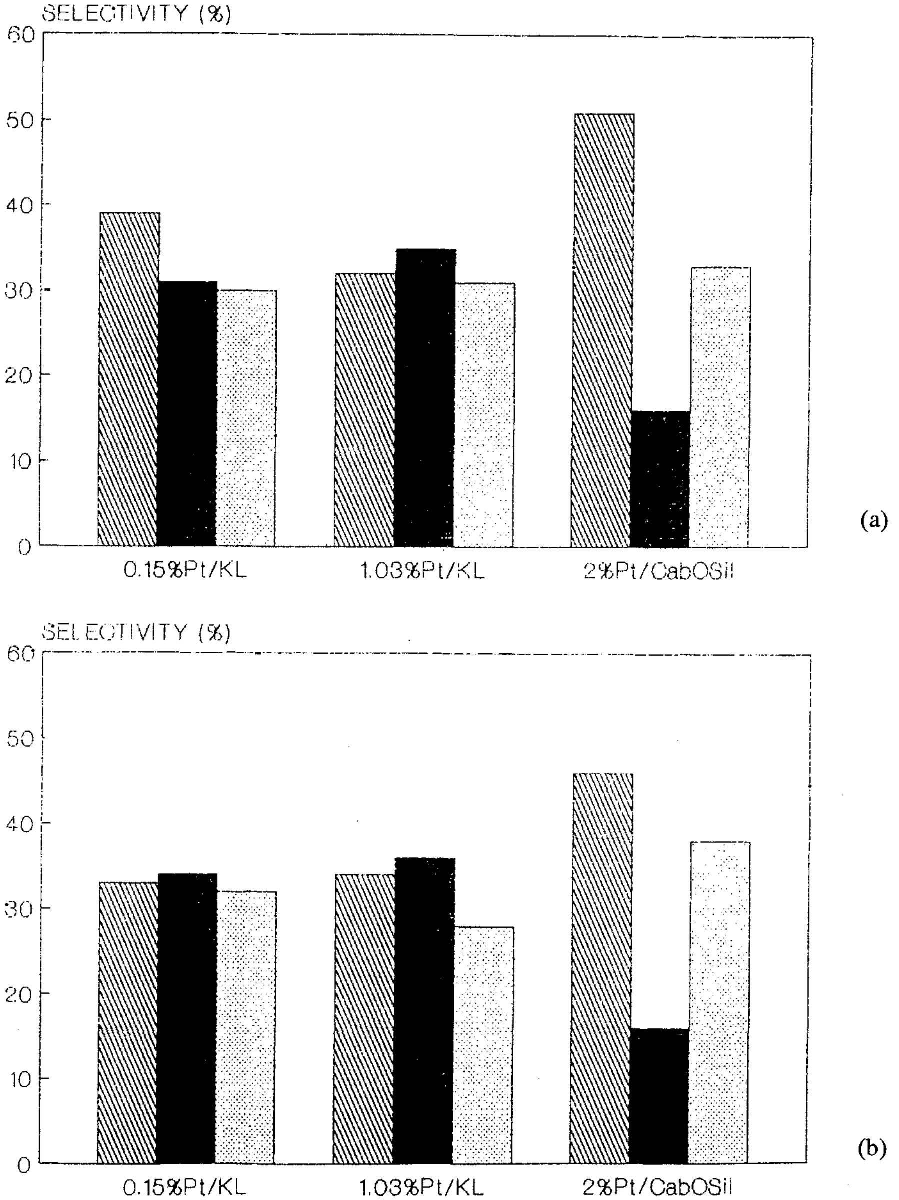

Fig. 1. Product distribution of MCP hydrogenolysis over Pt catalysts. Cross-hatched bars represent percentage of 2MP in the products; black bars, 3MP and shaded bars, n-hexane. a) comparison is made at constant overall conversion, 8%. b) comparison is made at constant temperature 533 K.

probing the state of metal surfaces. The original proposition of Gault [11] considered two possible reaction mechanisms: a non-selective pathway, in which the five C–C bonds in the ring have equal probability to be cleaved and a selective pathway, which would involve a multiply adsorbed species. The first reaction path would give a statistical product distribution, i.e. 3MP : 2MP : n-Hex = 1 : 2 : 2, while the selective path would mainly produce 3MP and 2MP. In both cases, the 3MP/2MP ratio is predicted to be 1/2. This has been experimentally confirmed, although 3MP/2MP values somewhat smaller than 1/2 have been commonly observed [12].

The first 3MP/2MP values significantly greater than 1/2 were reported by Sachtler et al. [13–15] who worked with Pt catalysts supported on NaY zeolites. They interpreted these unusual 3MP/2MP values in terms of the microgeometry of the system. They considered that the MCP molecules have a length/width ratio of about 1.7 and before reaching the Pt particles they have to diffuse through the pores of the zeolite. Therefore, the preferred orientation of these molecules through their diffusion path should be with their longer axis parallel to the direction of the pores. It can be expected that when these molecules reach the Pt particles, particularly those which completely fill the zeolite cages and pro-

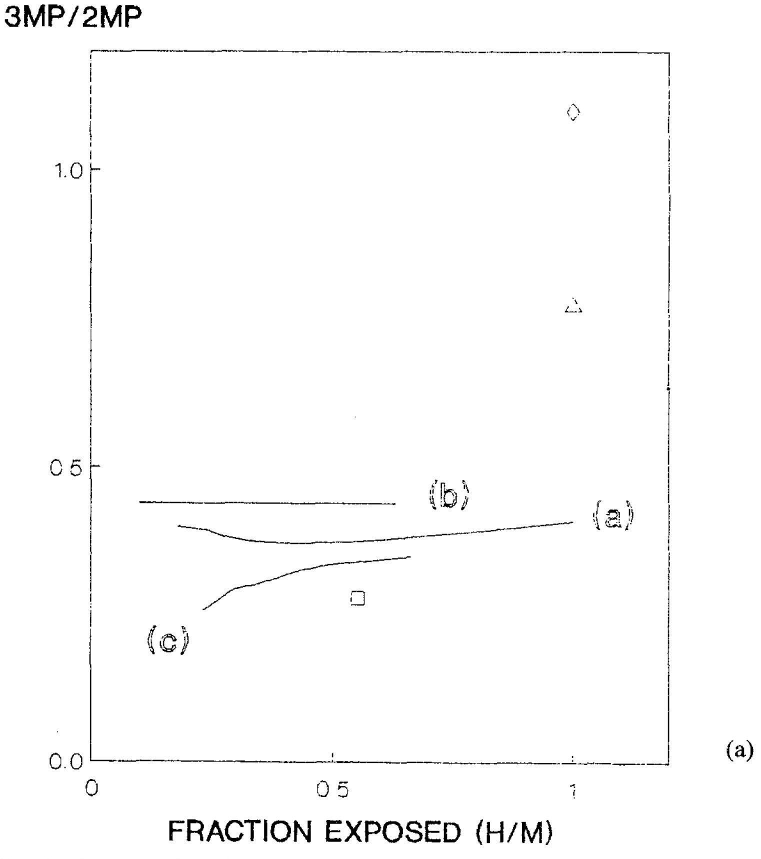

Fig. 2. Product distribution as a function of metal dispersion (fraction exposed) over Pt catalysts. Squares represent 2% Pt/CabOSil, diamonds 1.05% Pt/KL zeolite; triangles 0.13% Pt/KL zeolite. (a) 3MP/2MP ratio: curves a, b and c represent data from ref. [16a, b and c], respectively. (b) 3MP/n-Hex ratio: curves a, b and c represent data from ref. [16a, b and 12], respectively.

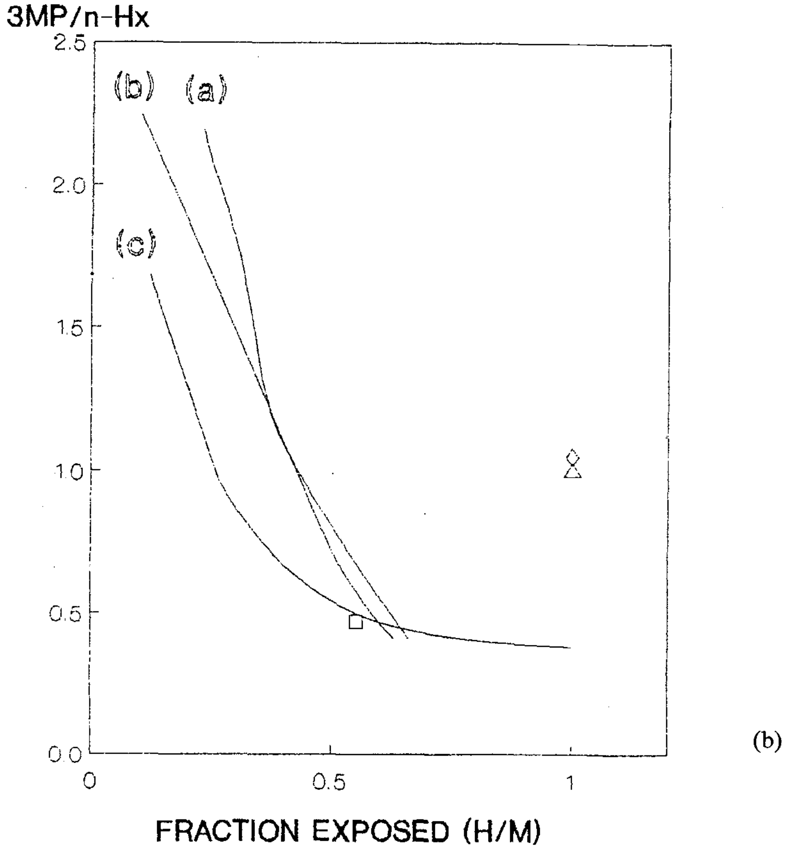

Fig. 2. (continued).

trude through the cage window, they should be preferentially cleaved through one of their ends, i.e., the flat bottom end or the methyl group end. Thus, it can be expected that the 3MP/2MP ratio be greater than the statistical value of 1/2 since the formation of 3MP should be favored in comparison to 2MP. This is indeed the case for our Pt/KL catalysts. The unusually high 3MP/2MP values are a clear example of the role that the collimating effects may have on hydrocarbon reactions on these catalysts, in good agreement with previous ideas [7].

It is important to note that the unusual product distribution obtained over our Pt/KL zeolite catalysts cannot be ascribed to mere particle size effects. This is demonstrated in figs. 2a and 2b. We have plotted the 3MP/2MP and 3MP/n-Hex values obtained on our catalysts, together with data from other authors [11,12,16], as a function of metal dispersion (fraction exposed). The data corresponding to our SiO_2-supported catalyst perfectly matches with the previous data. But, the 3MP/2MP and 3MP/n-Hex ratios, corresponding to the Pt/KL zeolites, are significantly greater than the predicted values for highly dispersed Pt. Then, it is clear that the production of 3MP is enhanced on these catalysts.

In principle, the collimating effects described above should not hinder the production of n-Hex relative to 3MP since we can expect that the approach to the metal with the methyl group end would be as probable as that with the flat bottom end. However, our data indicate that the 3MP/n-Hex ratios are higher than the statistical ratio of 1/2, and much higher than the predicted value for highly dispersed Pt. As discussed by Moretti and Sachtler [13] these results can also be explained by geometric arguments. Due to steric constraints the MCP molecule cannot rollover inside the cages containing the Pt particles. Consequently, only half of the molecules approaching the Pt through their methyl group end will have the H atom at the tertiary C pointing in the right direction to produce n-Hex. This result is another example of the important role played by the geometric effects on these catalysts.

On the other hand, it is interesting to compare the increased activity exhibited by the Pt/KL zeolite catalysts relative to the Pt/SiO_2 catalyst, the increase being more notorious on the higher loading Pt/KL catalyst.

This promoting effect has been previously observed. For example, similar increases in activity for MCP hydrogenolysis have been recently reported by Bai and Sachtler [17] for a Pt/Y zeolites series. They observed a clear trend in activity as the basicity of the zeolite was increased by alkaline ion exchange, with the K-containing catalyst exhibiting the higher activity.

The nature of the alkali promoting effect is still a matter of controversy. Some authors explain these effects in terms of long range interactions resulting from an electron transfer from the alkali to the metal [2,10,17]. This transfer would increase the electron density in the small metal particles and enhance their ability of donating electrons to the reacting molecules being adsorbed on their surface. Ponec et al. [18] have criticized this view proposing that the promoting action does not take place "through the metal" but rather by a local interaction in the neighbourhood of the alkali. This interaction would directly affect the binding characteristics of the reacting molecules on the metal surface. In this work we have observed that the activity enhancement is more pronounced for the 1.03% Pt/KL catalyst than for the 0.15% Pt/KL. This Pt loading effect can be used as an argument in favor of the local interaction approach. Inside the zeolite cages, the Pt particles must have about the same size in both catalysts (approx. 10 Å). Therefore, we can expect that the catalyst with the higher loading, i.e. with the higher density of Pt particles, may have a higher density of Pt particles in direct contact with the K cations, which are the same in both catalysts.

5. Conclusions

The analysis of product distribution and catalytic activity observed for the hydrogenolysis of MCP over Pt supported on KL zeolites indicate that both, geometric and promoting effects are important on these catalysts:

a) the enhanced production of 3MP obtained over these catalysts in comparison with SiO_2-supported catalysts illustrates the role of collimating (geometric) effects.

b) the increased activity exhibited by the KL zeolite-supported catalysts relative to SiO_2-supported ones indicates the existence of alkali promoting effects. This promotion would require a direct contact with K cations.

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