JOURNAL OF CATALYSIS **125**, 387–389 (1990)

Molecular Die Catalysis: Hexane Aromatization over Pt/KL

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Received December 18, 1989; revised April 23, 1990

INTRODUCTION

Although the aromatization of C_6 paraffins has been the subject of much research, selectivity for this reaction was, until recently, quite poor. This was abruptly changed by Bernard's discovery (*1*) that platinum supported on the K^+-exchanged form of zeolite L (Pt/KL) had much higher activity and selectivity for this reaction than previously known catalysts. In tests at 520°C and 203 psig, Pt/KL demonstrated twice the benzene yield obtained with a conventional Pt catalyst together with decreased (by 45%) production of light gas. This remarkable improvement in selectivity was confirmed in other laboratories (*2*).

Further studies of Pt/KL (*2*) revealed it to be monofunctional, meaning that all reactions occur at the platinum surface. Due to the nonacidic nature of the KL surface, metal–acid bifunctional synergism does not occur. Pt/KL is similar in this respect to Pt/SiO_2. However, as shown below, these two monofunctional catalysts greatly differ in their selectivity for hexane aromatization.

In this report we attempt to explain these properties, based on a model which explicitly involves the zeolitic nature of the carrier. (An abbreviated account was presented to the Materials Research Society (*3*)) This model was heavily influenced by the unusual cracking pattern exhibited by the Pt/KL catalyst. Such an influence would appear unlikely, since hexane cracking, at whatever position, rules out the subsequent formation of benzene. However, the cracking pattern suggested an explanation based on an unusual pattern of hexane adsorption at the platinum surface.

EXPERIMENTAL

One percent Pt/SiO_2 catalysts were prepared by impregnating SiO_2 with H_2PtCl_6 solution, followed by drying at 110°C. Pt/Kl (0.6–0.8% Pt) was prepared by exchanging zeolite L powder with $Pt(NH_3)_4Cl_2$ solution at room temperature for 20 h. After filtering, the catalyst was dried at 110°C, then calcined at 350°C for 3 h.

n-Hexane aromatization experiments were carried out at 510°C, 100 psig pressure, with a H_2/hexane mole ratio of 6. Space velocity was 50 w/w/h for the Pt/KL runs and 10 or 25 w/w/h for runs with Pt/SiO_2. Catalysts (20/40 mesh) were activated *in situ* with flowing H_2 at 510°C for 1 h before introducing liquid feed.

RESULTS AND DISCUSSION

Early in the course of these investigations, it became clear that there were two major differences between Pt/KL and the conventional monofunctional catalyst, Pt/SiO_2. As expected, we found Pt/KL to be far more selective (and active) for aromatization. In addition, the cracking patterns of the two catalysts contrasted sharply. Whereas Pt/SiO_2 yielded slightly *less* pentanes than butanes, with Pt/KL the C_5/C_4 molar ratio always exceeded unity and was

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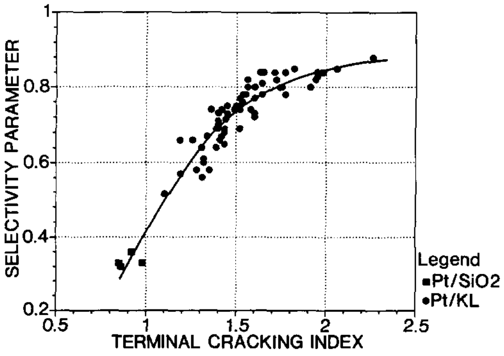

FIG. 1. Aromatization selectivity (defined in text) versus C_5/C_4 molar ratio.

often close to 2. This difference had nothing to do with the ratios of secondary/primary cracking, as shown, e.g., by experiments at different space velocities, but reflected the respective primary cracking patterns. Further studies revealed that Pt/KL's superior aromatization properties and unusual cracking pattern were, in fact, closely correlated.

This is shown in Fig. 1, in which selectivity for hexane aromatization is plotted against the C_5/C_4 molar ratio. "Selectivity" refers to a catalyst's ability to aromatize versus its tendency to crack. Due to uncertainties regarding the methane analysis, it is defined here as the yield ratio (benzene)/(benzene + C_{2-5}), where C_{2-5} is the sum of C_2 through C_5 and yields are expressed as weights percent. The data in Fig. 1 represent 32 runs with different Pt/KL catalysts and three with Pt/SiO_2. Data were collected 3–4 h after introduction of liquid feed. (The additional points in Fig. 1 refer to data collected with selected samples after a further 20–22 h.) Total yield of benzene plus cracked product was generally 20–40 wt%. The most selective Pt/KL catalysts were roughly 10 times as active for benzene formation, per gram of catalyst, as Pt/SiO_2.

Figure 1 suggests a simple explanation of the wide range of selectivities exhibited by the various Pt/KL samples. In such a catalyst there will be a distribution of platinum between *in-channel* and *out-of-channel* locations. For Pt/SiO_2, all the platinum is necessarily out-of-channel and this is associated with low values for both selectivity and C_5/C_4 ratio. (We will henceforth refer to the C_5/C_4 molar ratio as the "terminal cracking index" [TCI].) The most selective Pt/KL catalysts have high TCI values. As selectivity declines across this group of materials, the TCI declines as well, with Pt/SiO_2 appearing to be an "end-member" of the family of Pt/KL catalysts, i.e., an extrapolation of the Pt/KL data intersects the Pt/SiO_2 data. The implication is that as one follows the curve in Fig. 1 leftwards and downwards, an increasing proportion of the active platinum is located out-of-channel. These Pt/KL catalysts involved many different KL preparations, with subtle variations apparently affecting the platinum distribution.

Thus, in a well-prepared Pt/KL catalyst, a large proportion of the active platinum is located within the zeolite channel structure and such platinum is associated with high values for both aromatization selectivity and the terminal cracking index. This selectivity–TCI correlation is not explicable on the basis of a common diadsorbed intermediate. Hydrogenolysis is generally supposed to involve the coordination of two carbon atoms, in an α, γ configuration, to the metal surface, which cannot lead to a six-membered ring. However, if we focus on the initial *adsorption* of the *n*-hexane molecule on the platinum surface the correlation becomes clearer. If a molecule of *n*-hexane is coordinated through its terminal (C_1) carbon atom, it is possible that subsequent coordination of the C_6 carbon atom will occur, leading ultimately to benzene. (With a monofunctional catalyst, aromatization *must* involve 1,6-ring closure, since 1,5-closure followed by ring expansion requires carbonium ion activity.) Of course, terminal adsorption can have other outcomes, e.g., hydrogenolysis via 1,3-coordination or skeletal isomerization via 1,5-coordination.

However, *nonterminal* adsorption *cannot* lead to aromatization. Thus, if a catalyst were capable of inducing a greater probability of terminal, versus nonterminal, adsorption of *n*-hexane, an enhanced selectivity for aromatization should result. In addition, it is intuitively obvious that terminal adsorption will favor terminal cracking versus nonterminal cracking. We therefore propose that Pt/KL's high aromatization selectivity and high TCI are both the result of an enhanced probability of terminal adsorption of hexane at the platinum surface. We further propose that this altered pattern of adsorption is a geometric effect imposed by the zeolite structure.

Recent research has shown that neither Pt/KL's high aromatization selectivity nor its high terminal cracking index is unique (*4*). These properties have been achieved by treating faujasite, with an initial SiO_2/Al_2O_3 ratio <5, by a repeated sequence of acid leaching and steaming to produce a final SiO_2/Al_2O_3 ratio of about 40. This alteration substantially decreases the acidity. After Pt loading, the catalysts were tested for hexane aromatization under the same conditions as those used with Pt/KL. Both aromatization selectivities and TCIs were high. The data, in fact, conformed to the correlation shown in Fig. 1.

Clearly, the properties of Pt/KL cannot be related to its high potassium content, nor to details of its zeolite channel structure. KL and faujasite have orifices of 7.1–7.4 Å, formed by quasi-circular arrays of 12 O atoms. A molecule passing through this orifice will enter a 13-Å-diameter supercage in the case of faujasite or, in the case of zeolite L, a widened channel segment (cavity) of about 12 Å diameter. K^+ ions will reduce the effective cavity diameter to about 10 Å. Cavities/supercages that contain Pt are the reaction sites. As noted above, neither KL nor high-silica-faujasite are sufficiently acidic to promote bifunctional synergism with Pt; the latter is the sole source of activity. However, the fact that these Pt clusters are accessible only through portholes of ~7.3 Å has a profound effect, we believe, on their catalytic properties.

A possible explanation is that, since a butane molecule is ~7 Å long, longer paraffins will find it easier to pass through a 7.3 Å orifice lengthwise rather than transversely. Despite bent molecular conformations, it seems plausible that such an orientating effect should exist to some degree. A Pt cluster of even two-atom diameter inside a supercage will lie in the path of the entering molecule, leading to end-on attachment to the metal surface.

SUMMARY

Pt/KL contrasts with Pt/SiO_2 in having: (1) a much greater selectivity for hexane aromatization; (2) a strong preference for cracking the terminal carbon–carbon bond as opposed to interior bonds. These properties, taken together, suggest enhanced terminal adsorption of the hexane molecule at the Pt surface. Pt/high-silica faujasite has similar characteristics. We believe the fact that Pt in both these zeolites is accessible only through portholes of ~7.3 Å is a critical feature which leads to these unusual properties.

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