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The Nature of the High Sensitivity of Pt/KL Catalysts to Sulfur Poisoning

T. Fukunaga[1] and V. Ponec

Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

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Sulfur tolerance and selectivity changes caused by sulfur were investigated on Pt/KL, Pt/SiO_2, and Pt–K/SiO_2 catalysts for skeletal reactions of *n*-hexane and dehydrogenation of cyclohexane. Measurement of accessible Pt surface by CO and transmission electron microscopy (TEM) observations were also performed. The results showed that the presence of K^+ can be related to both the high aromatization activity/selectivity and the high sensitivity to sulfur poisoning in *n*-hexane conversion. The decrease in dehydrogenation activity (pure metallic function) caused by sulfur was more pronounced on K^+-free catalyst. It is suggested that K^+, which stabilizes an intermediate of aromatization, loses this property by its interaction with sulfur. Thus, significant and selective loss of aromatization activity occurs in the presence of sulfur.

INTRODUCTION

Pt/KL zeolite has attracted much attention in both fundamental and applied research since Bernard reported its very high activity and selectivity for aromatization of hexane (1). It is generally accepted that only Pt clusters catalyze the aromatization reaction and the acidic centers of the carrier, when present, decrease the selectivity, unlike the conventional Pt/Al_2O_3 reforming catalyst (1, 2). A unified and generally accepted explanation of the high activity and selectivity of the Pt/KL zeolite catalyst is not yet available, although some explanations have been put forward already: the confinement model (3), the end-on adsorption model (4, 5), and various electronic effects (6–9). A relation between the Pt^{n+}/Pt ratio and cyclization selectivity was earlier observed with the Pt/Al_2O_3 catalyst (10); an increasing cyclization selectivity was correlated with the increase in the Pt^{n+}/Pt. This (10) was another idea on how possibly to explain the extraordinary high cyclization selectivity of Pt/KL zeolites.

The industrial applications of the Pt/KL zeolite would probably be more numerous if one understood and could overcome the very high sensitivity to sulfur poisoning. Recently, two independent groups (11, 12) reached the same conclusion about sulfur poisoning. Vaarkamp *et al.* (11) claimed that the high sensitivity of the Pt/LTL catalyst to poisoning by sulfur can be attributed to the loss of active platinum surface by adsorption of sulfur and to the growth of Pt clusters. The growth of the Pt particles, observed by EXAFS, supposedly led to blocking of the pore mouths and significant loss of dehydrocyclization activity. McVicker *et al.* (12) also arrived at the conclusion that even a very low concentration of thiophene in the feed accelerates the agglomeration and subsequent deactivation of platinum.

In this study, the possible relation between Pt^{n+} and aromatization selectivity with Pt/KL was studied first. Then the mechanism of the aromatization reaction and sulfur poisoning in Pt/KL was investigated by comparing its catalytic behavior with that of Pt/SiO_2 and Pt–K/SiO_2. Although the size of the effects is not the same, the catalytic measurement and the characterization of three above-mentioned catalysts clearly show that the presence of K^+ can indeed be related to both the high aromatization activity/selectivity and the high sensitivity to sulfur poisoning.

METHODS

Catalyst Preparation

Pt/KL (1 wt%) was prepared by the incipient wetness impregnation method. KL zeolite powder (from UOP), dried in an oven at 373 K for 3 h, was impregnated with an aqueous solution of $Pt(NH_3)_4Cl_2$ with stirring. The impregnated KL was dried first at room temperature for 1 h and then at 373 K for 3 h in a drying oven, followed by calcination in flowing O_2 at 573 K for 3 h.

For the preparation of Pt/SiO_2 (1 wt%) Aerosil 200 (Degussa) and $Pt(NH_3)_4Cl_2$ were used. After incipient wetness impregnation the solid was kept at room temperature for 1 h; water was then slowly removed on a hot-water bath up to almost dryness. Subsequent drying in the oven and calcination were performed under the same conditions as employed for Pt/KL.

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[1] On leave from Idemitsu Kosan Co. Ltd., Japan.

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Pt–K/SiO_2 (1 wt%) was prepared in the same way as for Pt/SiO_2 except that $Pt(NH_3)_4Cl_2$ and K_2CO_3 were coimpregnated onto the carrier.

Pt/Al_2O_3 (1 wt%) was also prepared using $PtCl_4$ impregnated onto Aluminiumoxyd C (Degussa). The method of preparation was the same as that for Pt/SiO_2.

Determination of Pt^{n+} Ions in Pt/KL

This method consists of two steps: (1) an *in situ* extraction of Pt^{n+} ions from a reduced catalyst and (2) a determination of Pt^{n+} in the extract.

The *in situ* extraction was performed under reflux conditions for 16 h at 413 K using the liquid of 4 vol% acetic acid (HAc) in ethylenediamine ([en]). The extract was then separated from the remaining catalyst by filtration. The residue was washed three times by the new HAc/[en] liquid and the total volume was brought to 25 ml. These procedures were the same as those applied by Botman *et al.* (10), except that we performed filtration rather than centrifugation for the separation of the extract from the catalyst. Atomic absorption spectroscopy (AAS, Perkin–Elmer 3100) was used for the detection of extracted Pt^{n+}.

Sulfurization

The catalyst was reduced *in situ* at 773 K for 4 h in flowing hydrogen prior to sulfurization. A thiophene/ethanol liquid mixture was then injected at room temperature into the gas stream. After the catalyst was kept at ambient temperature for 1 h, a reduction by hydrogen at 673 K for 1 h was conducted to remove hydrocarbon fragments adsorbed on the catalyst. The amount of sulfur introduced was expressed by the S/Pt ratio, where S is the amount of injected sulfur (mol-S/wt-cat.) and Pt is the Pt loading (mol-Pt/wt-cat.). Since the S/Pt ratio was not determined in the catalysts used, in all cases mentioned below we refer to a *nominal* ratio.

Reaction of n-Hexane

Skeletal reaction of *n*-hexane (n-C_6) was carried out using a fixed-bed quartz reactor at 673 K and atmospheric pressure. In a standard experiment, 0.02 g of catalyst was mixed with 0.98 g of fine granular quartz (0.2–0.8 mm, from Merck Co.). The H_2/n-C_6 molar ratio was kept at 16, and the total flow rate of gases was 20 ml/min.

Prior to study of the reaction, an *ex situ* reduction was carried out in flowing hydrogen (20 ml/min) at 773 K for 4 h followed by an *in situ* reduction at 673 K for 1 h in a 20 ml/min flow of hydrogen. However, the sulfurized catalyst was reduced only *in situ* at 673 K for 1 h, since hydrogen reduction at 773 K for 4 h had been performed before the sulfurization. The temperature ramping rate was 8 K/min in each case.

Analysis of products were performed by a gas chromatograph (Packard Model 429) equipped with a capillary column of 0.53 mm inside diameter, 25 m length, and CP-Sil-5 CB (Chrompack) stationary phase. Peak areas were used for the determination of the concentrations. The values of detection factors were used according to Purnell (13). The conversion (α), selectivity (S), and yield (Y) were calculated by

$$\alpha(\%) = \left(1 - \frac{n\text{-C}_6 \text{ weight in effluent}}{n\text{-C}_6 \text{ weight in feed}}\right) \times 100$$

$$S(\%) = \frac{\text{Each hydrocarbon weight in effluent}}{(n\text{-C}_6 \text{ weight in feed}) - (n\text{-C}_5 \text{ weight in effluent})} \times 100$$

$$Y(\%) = \frac{\text{Each hydrocarbon weight in effluent}}{n\text{-C}_6 \text{ weight in feed}} \times 100.$$

Dehydrogenation of Cyclohexane to Benzene

Dehydrogenation of cyclohexane (c-C_6) to benzene (Bz) was performed at 573 K, at atmospheric pressure, with H_2/c-C_6 molar ratio of 16 and total flow rate of 20 ml/min. The same reactor and the same amount of catalyst were used for this reaction as for the n-C_6 reaction. Pretreatment conditions and product analysis condition were also the same as those described above.

CO Adsorption

The Pt dispersion of the catalysts was estimated from the CO adsorption. For this purpose, a Quantasorb flow apparatus (Quantachrome) was used. After an *ex situ* reduction in a quartz reactor, the catalyst was passivated slowly by air and taken out. Then about 0.1 g of the catalyst was placed in the measurement cell and was reduced again *in situ* by flowing hydrogen at 673 K for 1 h. The extent of CO adsorption was determined by injecting 0.1-ml pulses of CO into a hydrogen flow at room temperature. The CO in the effluent gas was detected by a thermal conductivity detector (TCD), coupled to an integrator. The injection continued until the saturation of Pt metal surface had been reached, indicated by a constant CO amount in the effluent. The CO/Pt values determined in this way in the flow apparatus are lower than the values obtained under static conditions; however, it is not the absolute values of this ratio but rather the comparison of values for the various catalysts that will be considered here.

Electron Microscopy Measurement

Investigation of the effect of sulfur on the particle size distribution has been also carried out for Pt/KL, Pt/SiO_2, and Pt–K/SiO_2 using a transmission electron microscope (TEM). TEM images were obtained on a Siemens Elmiskop 102 instrument operating at 100 kV.

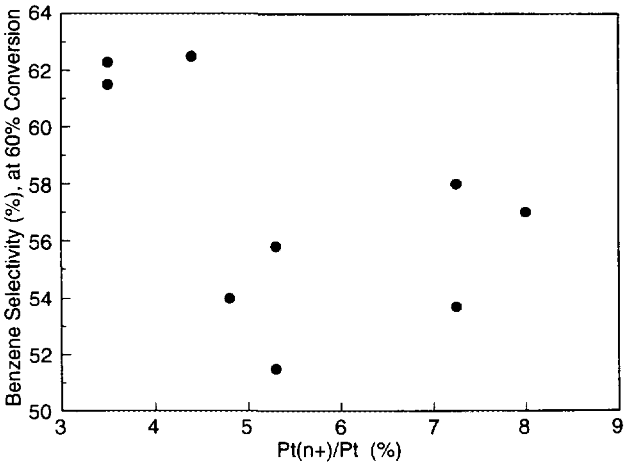

FIG. 1. Pt^{n+} concentration and aromatization selectivity of Pt/KL zeolites reduced under different conditions. Reaction conditions: 673 K; time on stream, 120 min. Conversion was adjusted to 60% by changing the total flow rate.

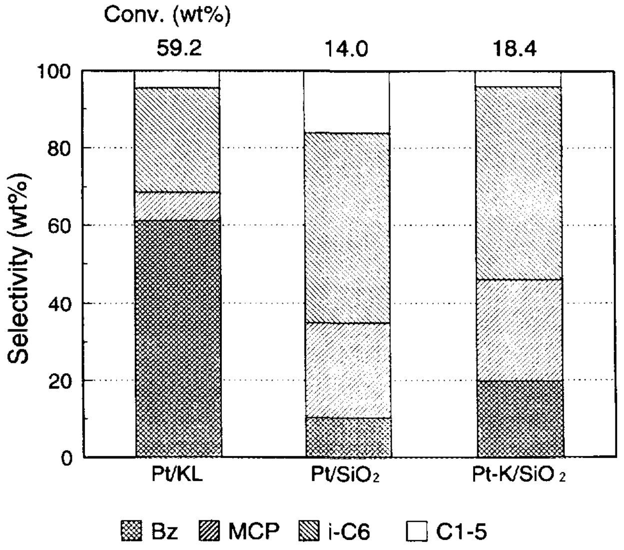

FIG. 2. Effect of K^+ in the catalyst on the n-C_6 reactions. Standard reaction conditions: 673 K; time on stream, 120 min for Pt/KL, 30 min for Pt/SiO_2, and Pt–K/SiO_2.

RESULTS

Possible Role of Pt^{n+} in Pt/KL

To investigate the possible role of Pt^{n+} in the n-C_6 aromatization, the Pt^{n+} content in Pt/KL was varied by changing the reduction conditions, viz. reduction time and reduction temperature, in the ranges 1–4 h and 673–773 K. The benzene selectivity on catalysts reduced in this way is shown as a function of Pt^{n+}/Pt in Fig. 1. At first sight, there is no correlation, contrary to what was expected according to Ref. (10).

Effect of K^+ on Aromatization Tested with Pt/SiO_2

Conversion and product distribution in n-C_6 reaction with Pt/KL, Pt/SiO_2, and Pt–K/SiO_2 are illustrated in Fig. 2. Deactivation occurred with Pt/SiO_2 and Pt–K/SiO_2, and therefore, the "initial" results, namely values obtained at a time on stream of 30 min, are shown here. Whereas no deactivation was observed with Pt/KL during the reaction, a self-poisoning was observed with the silica-supported catalysts. An addition of K^+-promoting compound to Pt/SiO_2 caused an increase in the selectivity to Bz and a decrease in the selectivity to C_{1-5}. Although the effects are not the same in their size, the presence of K^+ changes the catalytic properties of Pt/SiO_2 in the direction of the behavior of Pt/KL; i.e., it causes a higher aromatization activity and selectivity.

Influence of Sulfur on n-C_6 Reactions

The sulfur sensitivity of Pt/KL was studied by changing the (nominal) S/Pt ratio and comparing the results with those obtained with the Pt/Al_2O_3 catalyst (Fig. 3). A more significant decrease of n-C_6 conversion (total yield of Bz, methylcyclopentane [MCP], i-hexane [i-C_6], and C_{1-5}) with increasing S/Pt was observed for Pt/KL than for Pt/Al_2O_3. Inter alia, this confirms the results in Refs. (2, 11, 12). It is worthwhile mentioning that the significant loss of n-C_6 conversion on Pt/KL mainly resulted from the decrease in the Bz yield.

The selectivities to Bz and to C_{1-5} are plotted as a function of n-C_6 conversion for various Pt/KL catalysts having different nominal S/Pt ratios in Figs. 4 and 5, respectively. The catalysts of higher S/Pt showed the lower Bz selectivity and higher C_{1-5} selectivity when compared at the same conversion.

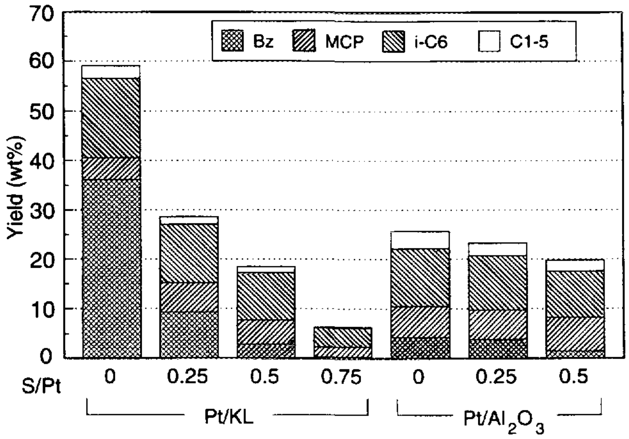

FIG. 3. Sensitivity of the Pt/KL and Pt/Al_2O_3 catalysts for sulfur poisoning, in n-C_6 reactions. Standard reaction conditions: 673 K; time on stream, 120 min.

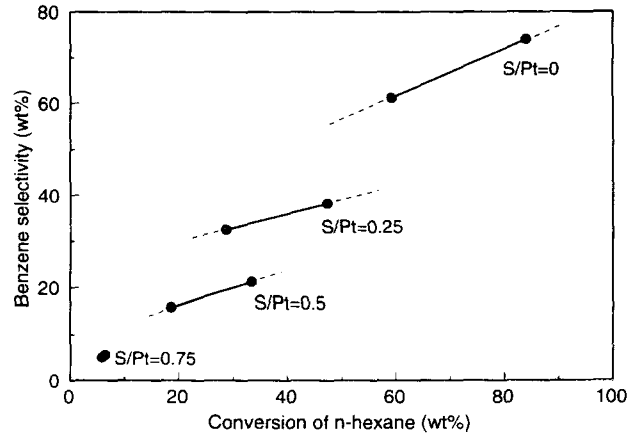

FIG. 4. Changes in the Bz selectivity of the Pt/KL catalysts. Changes caused by sulfur, in n-C_6 reactions. Standard reaction conditions: 673 K, flow(H_2 + n-C_6) = 20 or 10 ml/min.

The influence of sulfur on n-C_6 reactions with Pt/KL, Pt/SiO_2, and Pt-K/SiO_2 catalysts is summarized in Table 1. The S/Pt (nominal) ratio of sulfurized catalyst was 0.5 for all catalysts. The conversion and Bz yield (Y_{Bz}) were suppressed by sulfur with each catalyst, as expected. To express the extent of suppression quantitatively, we define the rate of the decrease in the Bz yield, $D(Y_{Bz})$, as

$$D(Y_{Bz}) = \frac{(Y_{Bz}\text{ of unsulfurized cat.}) - (Y_{Bz}\text{ of sulfurized cat.})}{Y_{Bz}\text{ of unsulfurized cat.}}.$$

The rate of the decrease in the Bz selectivity $D(S_{Bz})$ was defined similarly as

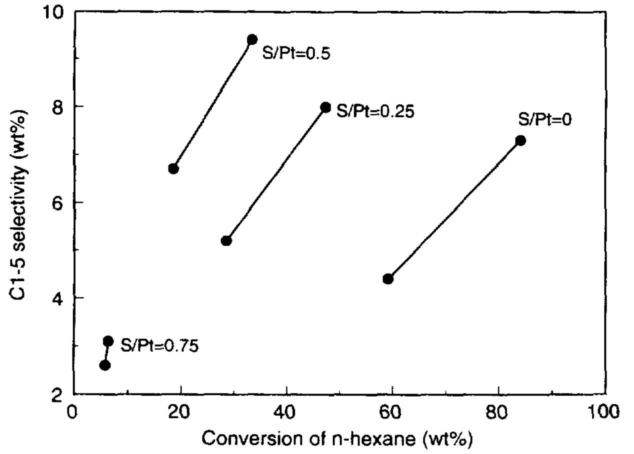

FIG. 5. Changes in the $C_{1\text{-}5}$ selectivity of the Pt/KL catalysts. Changes caused by sulfur, in n-C_6 reactions. Standard reaction conditions: 673 K, flow(H_2 + n-C_6) = 20 or 10 ml/min.

$$D(S_{Bz}) = \frac{(S_{Bz}\text{ of unsulfurized cat.}) - (S_{Bz}\text{ of sulfurized cat.})}{S_{Bz}\text{ of unsulfurized cat.}}.$$

$D(Y_{Bz})$ followed the order

$$\text{Pt/KL (92)} > \text{Pt-K/SiO}_2\text{ (86)} > \text{Pt/SiO}_2\text{ (79)},$$

and $D(S_{Bz})$ the order

$$\text{Pt/KL (74)} > \text{Pt-K/SiO}_2\text{ (73)} > \text{Pt/SiO}_2\text{ (67)},$$

where the figures in parentheses are the values of $D(Y_{Bz})$ and $D(S_{Bz})$, respectively. All these results suggest that the K^+-containing catalysts, i.e., Pt/KL and Pt-K/SiO_2, are more sensitive to sulfur poisoning than a catalyst without potassium promoter.

Sulfur also caused a change in the product distribution, with all catalysts studied. A decrease in the Bz selectivity and an increase in both the i-C_6 and MCP selectivities were the common phenomena. However, the changes in the $C_{1\text{-}5}$ selectivity seemed to depend on the presence of K^+: after the sulfur addition, the $C_{1\text{-}5}$ selectivity increased with K^+-containing catalysts, whereas it decreased with K^+-free Pt/SiO_2 catalyst.

Influence of Sulfur on Dehydrogenation of c-C_6 to Bz

Figure 6 shows the dehydrogenation activity of c-C_6 to Bz on sulfurized and unsulfurized catalysts. Suppression of dehydrogenation activity by sulfur was in the order Pt/SiO_2 > Pt/KL > Pt-K/SiO_2. It is very interesting that suppression of dehydrogenation activity (the "metallic" function) by sulfur was more pronounced on the K^+-free catalyst, while suppression of the n-C_6 aromatization was more pronounced on the K^+-containing catalysts (Table 1). This indicates that K^+ is somehow involved in aromatization. Neutralization of acid centers is not the only function of K^+ promoter.

CO Adsorption Measurements

The extent of decrease in the Pt surface area, as observed after sulfur poisoning and reflected by CO adsorption, is smaller than Pt/KL and Pt-K/SiO_2 than with Pt/SiO_2 (Fig. 7). This decrease corresponds well with the extent of the suppression of the dehydrogenation activity (Fig. 6), but not with that of aromatization activity (Table 1).

TEM Observations

The Pt particle size distribution was observed by TEM for sulfurized and unsulfurized catalysts. Neither the average particle size nor the particle size distribution was changed by sulfur for Pt/SiO_2 (Figs. 8a and 8b) or Pt-K/

TABLE 1

Influence of Sulfur on n-C_6 Reactions[a] with Pt/KL, Pt/SiO_2, and Pt–K/SiO_2

Catalyst	Conv. (wt%)	Bz yield (wt%)	Selectivity (wt%)				
			$C_{1\text{-}5}$	i-C_5	MCP	Bz	Others
Pt/KL[b]	59.2	36.2	4.5	27.0	7.4	61.1	tr
S–Pt/KL[b,c]	18.5	3.0	6.7	51.4	25.9	15.9	0.1
Pt/SiO_2[d]	14.0	1.4	16.2	48.1	24.8	10.2	0.7
S–Pt/SiO_2[c,d]	8.4	0.29	14.5	54.0	26.5	3.4	1.6
Pt–K/SiO_2[d]	18.4	3.6	4.1	50.0	26.1	19.8	tr
Pt–K/SiO_2[e]	15.5	2.9	3.5	50.2	27.8	18.4	0.1
S–Pt–K/SiO_2[c,d]	8.2	0.40	6.1	56.2	31.4	4.9	1.4

[a] Standard reaction conditions: 673 K, flow (H_2 + n-C_6) = 20 ml/min.
[b] 120 min time on stream.
[c] S/Pt = 0.5.
[d] 30 min time on stream.
[e] 45 min time on stream.

SiO_2 (Figs. 9a and 9b). This supports the idea that changes in the aromatization selectivity of $Pt/K/SiO_2$ catalysts caused by sulfurization are not due to particle size growth. It has been shown in the literature (11, 12) that the particle size of Pt–KL catalysts grows by sulfurization and this was related (11, 12) to the variation in the aromatization selectivity. However, our interpretation of the present results is that changes observed in aromatization due to sulfur added to Pt–K/SiO_2 are not due to particle size changes.

DISCUSSION

Possible Role of Cations in the Aromatization

It has been proposed that Pt^{n+} stabilizes the intermediate (perhaps an allyl-like species) for cyclization, leading to a high selectivity of dehydrocyclization with Pt/Al_2O_3 catalysts (10). Survival of Pt^{n+} after a reduction in a zeolite system could be even more probable than with Al_2O_3 or SiO_2; the presence of Pt^{n+} was indeed observed in reduced Pt/KL zeolite by Kappers and van der Maas (14), who used the IR spectrum of adsorbed CO as a probe. We therefore investigated first the possible role of Pt^{n+} in the n-C_6 aromatization.

Aromatization selectivity depends on n-C_6 conversion (15–18): Bz selectivity increases with conversion, and accordingly the Bz selectivities on Pt/KL were compared here at the same conversion level of 60 wt% and plotted against Pt^{n+}/Pt in Fig. 1. At first, no correlation between the Bz selectivity and the Pt^{n+}/Pt ratio was found at a constant total conversion of n-C_6. This result caused us to abandon the idea but a closer inspection of the results and conclusions in the papers by Miller *et al.* (19) and Vaarkamp *et al.* (20) has led us to a second thought on this subject, namely the following one. The mentioned authors (19, 20) discovered that the samples reduced at low temperature contain hydrogen between Pt particle and

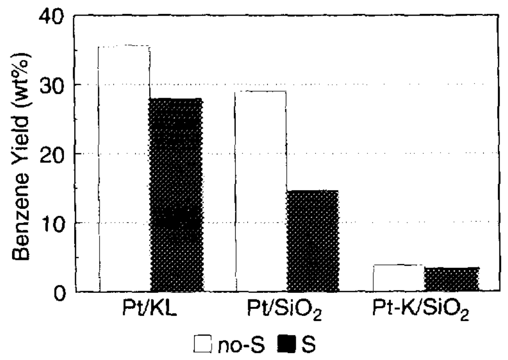

FIG. 6. Influence of sulfur on dehydrogenation of c-C_6 to Bz. Standard reaction conditions: 573 K; flow(H_2 + c-C_6) = 20 ml/min; time on stream, 120 min; S/Pt of all sulfurized catalysts = 0.5.

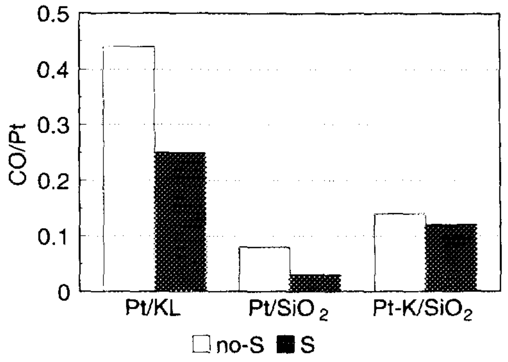

FIG. 7. Changes in the Pt surface caused by sulfur. Poison-free Pt surface is defined by the CO/Pt_{total} ratio, determined in a standard flow measurement; S/Pt of all sulfurized catalysts = 0.5.

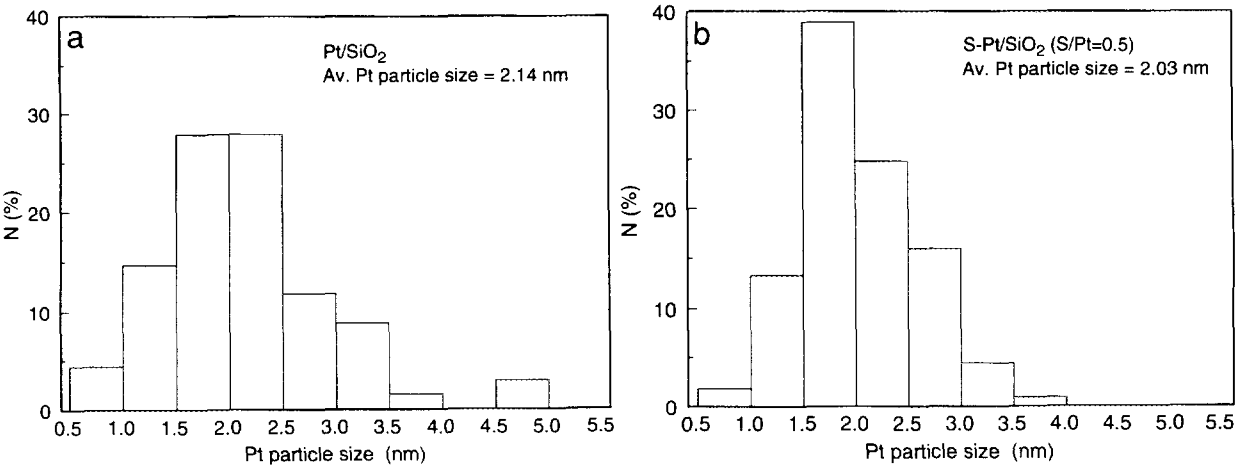

FIG. 8. Pt particle size distribution on (a) Pt/SiO$_2$ and (b) sulfurized Pt/SiO$_2$ (S/Pt = 0.5).

zeolite, causing the Pt particle to be at a greater distance from the oxide framework (which could mean also a greater distance from Pt^{n+} or K$^+$). Thus the samples in Fig. 1, analyzed and tested for Pt^{n+} and aromatization, differ simultaneously in two respects: the extent of Pt^{n+} survival (a positive effect, possibly the right part of Fig. 1) and the extent of the retained hydrogen (a negative effect). Only at the highest reduction temperature is the effect (if any) of Pt^{n+} free from the negative effect of adsorbed hydrogen. This could be the case, but because of the obviously present complication due to the retained hydrogen we did not see much promise in pursuing the research in that direction. Instead, we turned our attention to the other ions present in the cages, the potassium ions.

The effect of K$^+$ was then studied with monofunctional Pt/SiO$_2$ catalyst, with which we attempted to simulate the role of K$^+$ in the Pt/KL catalyst. Figure 2 shows the promotion effect of K$^+$ on the n-C$_6$ aromatization. Such an effect of an alkali metal on hydrocarbon conversion was actually already demonstrated earlier by, e.g., McCarroll (21), who reported that the yield of Bz from n-C$_6$ increased by a factor of 2.5 times over Pt/graphite catalyst at a sodium doping level of 200–300 ppm. Thus the beneficial effect alone of added alkalis seems to be well established. The more difficult task is to explain the effect.

Explanations based on an assumed electron transfer, either from platinum to a Lewis acid center or from a Lewis base center to platinum are very popular in the literature [see, e.g., Refs. (6–9)]. However, there are some reasons not to accept these ideas unquestioningly. First, a transfer of an electron from alkali ion *to* platinum, to make it electron rich, is excluded (the second ionization potential of K is 31.8 eV) and a transfer from the lattice oxygen or from the –OK group is not very likely. The probability of

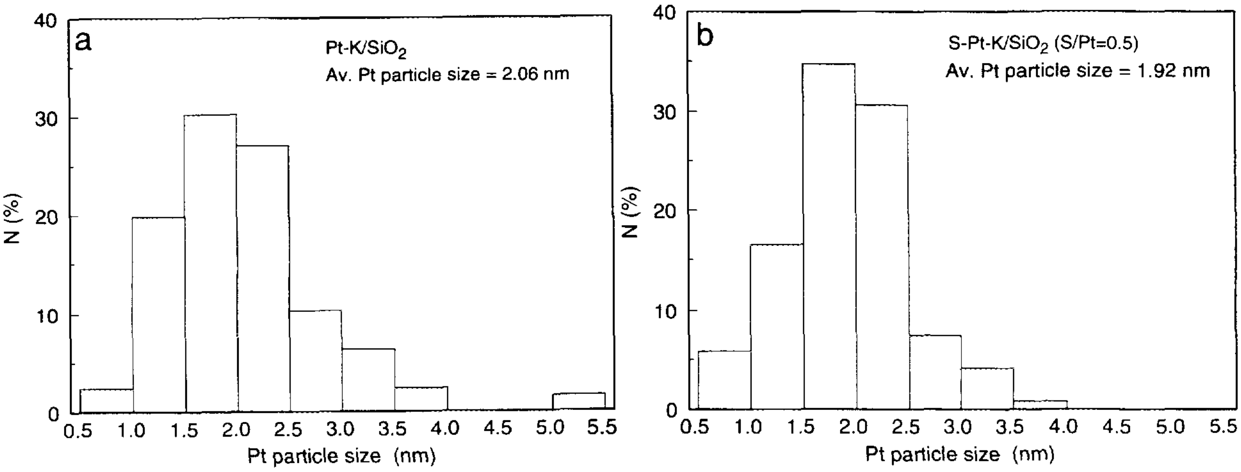

FIG. 9. Pt particle size distribution on (a) Pt–K/SiO$_2$ and (b) sulfurized Pt–K/SiO$_2$ (S/Pt = 0.5).

an electron transfer *from* platinum to the Lewis acid center of a zeolite is not known but let us compare two quantities, namely the work function of platinum, which is (depending on the crystal plane considered) 5.5–6.0 eV and the thermionic work function of Al_2O_3, which is 4.7 eV, so that the lowest lying acceptor level of Al_2O_3 should be at about 3.7–2.7 eV. This does not favor electron transfer from Pt^0 to Al^{3+}. However, let us accept that there is one electron already transferred (in whatever direction) between a Pt particle with, say, 13 atoms and the zeolite lattice. Then the question is how should this single electron influence the (say) 13 atoms of the particle, when we know that such a particle shows already a quite efficient screening of charges (22) and with metallic screening the electrostatic field does not spread from the charge transferred through the rest of the metal particle [for the estimation of that, see Refs. (23, 24)]. When we abandon the idea of electron transfer effects, we have to turn to other possibilities. Among them the most likely is that the electric charges in cations or anions can produce such an electrostatic field that the intermediates on the metal particles can be influenced by a through-the-vacuum effect. This electrostatic field effect is well documented for syngas reactions (25–29), and we suggest that it is operating here, too. The geometry of the platinum–K^+ interaction in cages of KL zeolite is obviously more favorable for the stabilization of intermediates of an aromatization than that in the Pt–K/SiO_2 catalyst. Additionally, the lifetime of molecules (intermediates) in this field is longer in the Pt/KL zeolite than in the Pt–K/SiO_2 catalyst.

Sulfur Poisoning in n-C_6 Reactions

If sulfur, when being added in increasing amounts, were successively poisoning an increasing amount of otherwise equivalent sites, one would expect one common curve for $S_{Bz} = f$(contact time) or $S_{Bz} = g$(conversion), a curve like that in Fig. 8 of Ref. (12). However, the points in our Fig. 4 do not lie on a common curve and in our opinion this is an indication that sulfur is subsequently poisoning sites of different quality. The higher $C_{1\text{-}5}$ selectivity we observed with sulfurized Pt/KL (up to S/Pt = 0.5 in Fig. 5) is in good agreement with the results reported by Vaarkamp *et al.* (11). The increase in the hydrogenolysis selectivity can be considered as a strong indication that the activity loss observed after sulfurization of Pt/KL (and also of Pt–K/SiO_2) is not due to a simple ensemble size decrease by sulfur adsorption, because hydrogenolysis that requires large ensemble size should have been suppressed preferentially (30), if the ensemble size decrease were the only reason for the change in the selectivity. On the other hand, the hydrogenolysis selectivity decrease by sulfur on Pt/SiO_2 probably *is* due to the average ensemble size decrease. Thus, the presence of K^+ seems to change the sulfur poisoning mechanism.

Sulfur Poisoning in Dehydrogenation of c-C_6 to Bz

Dehydrogenation of c-C_6 has been described as a structure-insensitive reaction (31) and only a small ensemble is usually considered to be involved in the rate-determining step of the dehydrogenation reaction (32). In this sense, the activity (Bz yield) in Fig. 6 should reflect the changes in the accessible Pt surface area of the catalysts.

First, we make a comparison between the unsulfurized Pt/SiO_2 and Pt–K/SiO_2. The activity is much lower for Pt–K/SiO_2 (Fig. 6), whereas the CO/Pt ratio is higher (Fig. 7). Furthermore, the average Pt particle size determined by TEM is essentially the same for both catalysts (Figs. 8a and 9a). An interpretation that meets the experimental results is that the incorporated K^+ in Pt/SiO_2 is deposited on the Pt surface in the form of K_2O or KOH, causing Pt surface area loss without any change in the particle size distribution. The activity loss in the dehydrogenation reaction would be another indication of this. On the other hand, the increase in the amount of adsorbed CO can possibly be attributed to small changes in the particle size distribution or to an enhanced Pt–CO bond strength in the presence of a nearby K^+.

The aromatization can be promoted by K^+ in Pt/SiO_2 (Fig. 2 and Table 1), irrespective of the intrinsic Pt surface area loss. The much lower dehydrogenation activity of Pt–K/SiO_2, contrasting its aromatization activity higher than that of Pt/SiO_2, also indicates that dehydrogenation is not the rate-determining step of the dehydrocyclization (aromatization) reaction. Most probably the presence of K^+ promotes the closure of the ring.

Concerning the sulfur poisoning, the following can be said. The decrease in the dehydrogenation activity (Fig. 6) corresponds well with the decrease in the Pt surface area monitored by CO adsorption (Fig. 7). This could be expected because the dehydrogenation reaction is likely to be structure insensitive (31, 32), as already mentioned. What should be noted is that the K^+-free catalyst is *more sensitive* to sulfur poisoning in the dehydrogenation (metal alone function) although it is *less sensitive* in the *n*-C_6 aromatization. A possible reason for this is discussed in the next section.

Possible Mechanism of Sulfur Poisoning

Two recent papers (11, 12) claimed that the very high sensitivity of Pt/KL to sulfur poisoning is caused by the agglomeration of Pt particles and the subsequent blockage of KL zeolite channels by Pt particles. Our TEM observation of Pt particle size changes was not conclusive with Pt/KL zeolite. An increase in the $C_{1\text{-}5}$ selectivity of the sulfurized Pt/KL catalyst in the *n*-C_6 reaction (Table 1) could be expected if the particle growth by sulfur was observed. However, the much smaller decrease in the c-C_6 dehydrogenation activity (Y_{Bz} from 35.6 to 27.9%) by sulfur poisoning than that in the aromatization of n-C_6 (Y_{Bz} from 36.2 to 3.0 wt%) is not compatible with the agglomeration mechanism. Both reactions produce the same product (Bz), and hence, the blockage of KL zeolite channels and the subsequent diffusion hindrance (if there were any) should have influenced both reactions to the same extent. Further, only Bz formation was significantly suppressed and the formation of MCP, i-C_6, and $C_{1\text{-}5}$ were influenced little by sulfur (Fig. 3), suggesting that the simple loss of active sites by particle agglomeration is not the main cause of the aromatization activity loss.

It is very interesting that the K^+-promoted Pt/SiO_2 catalyst behaves like the Pt/KL catalyst with regard to sulfur poisoning. It seems that the existence of K^+ is related to the extent of sulfur poisoning. According to some papers, the electronic structure of Pt can be changed by alkali metals (6–9), and consequently the sulfur tolerance may change, too. Electron-deficient metal particles are claimed to show a better sulfur resistance (33–39); thus the electron-rich metals should be less resistant. Let us consider for a moment that the K^+-promoted catalysts do in fact contain electron-rich Pt particles and thus are less sulfur tolerant. Indeed, this idea would agree with our findings and those of others that the K^+-containing catalysts (Pt/KL and $Pt\text{-}K/SiO_2$) are more sensitive than the K^+-free Pt/SiO_2 to sulfur, as far as the aromatization reaction is concerned. However, the same K^+-containing catalysts are less sensitive to sulfur when in the dehydrogenation reaction. This is not what one would expect if the electron structure changes in Pt due to K^+ were the only reason for the changes in the catalytic behavior. Indications that the explanation of the extraordinary properties of the Pt/KL catalyst should not be based on the assumed changes in the electronic structure of Pt by the K^+ or other constituents of the zeolite were presented above. We can add here that the explanation of the effect of sulfur should not be looked for in that direction. Instead, let us consider the following point. The decrease by sulfur of the amount of surface adsorbing CO is smaller in the presence of K^+ than without K^+ in the catalyst, just as if a part of sulfur was bound somewhere other than to the Pt particles, namely to potassium. A beneficial effect of K^+ in the stabilization of the intermediates of aromatization and the blockage of K^+ by sulfur would explain all phenomena discussed up to this point.

Summarizing, we propose a picture of the sulfur poisoning as shown in Fig. 10. On Pt/SiO_2, sulfur poisons only the Pt particles, by changing the ensemble size distribution. The decrease in the selectivity for hydrogenolysis (a reaction that requires a large ensemble size) is an indication of this. On $Pt\text{-}K/SiO_2$ and Pt/KL, K^+ stabilizes an intermediate of aromatization, leading to a high and selective Bz formation from n-C_6. However, interaction between K^+ and sulfur reduces the stabilization ability of K^+ and hence induces a significant loss of aromatization activity in the presence of sulfur. This suppression of the Bz formation then results in a relatively high hydrogenolysis selectivity. Dehydrogenation, which takes place on Pt without being influenced by K^+, is less suppressed by sulfur on K^+-containing catalysts, because some part of sulfur added is adsorbed on K^+.

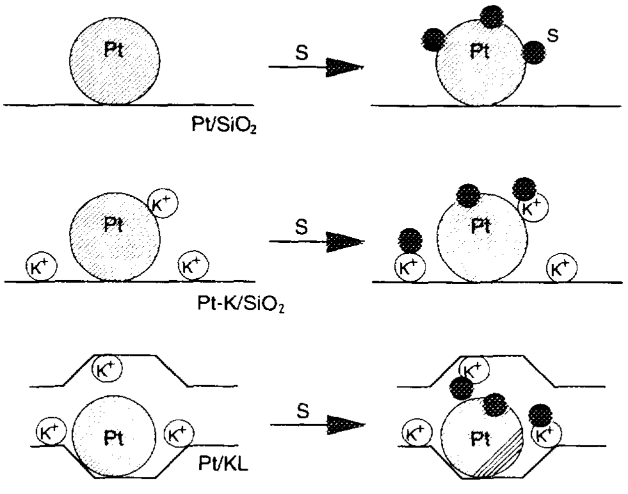

FIG. 10. A possible mechanism of the sulfur poisoning.

A possible strong interaction between sulfur and K^+ additives has already been reported (33, 40). Zubova *et al.* (40) suggested the formation of K_2S or KHS from sulfur compounds, with K_2O or KOH-promoted Fe catalysts for the ammonia synthesis. Barbier *et al.* (33) showed that K/Al_2O_3 (no transition-metal present) retains H_2S more strongly than pure Al_2O_3 or chlorinated Al_2O_3, and an appreciable amount of sulfur remains adsorbed on K/Al_2O_3 even at a temperature higher than 773 K. The stronger bond strength between sulfur and potassium than between sulfur and platinum can also be expected from thermodynamic data (41), as the following reaction enthalpy considerations (298 K) show:

	Pt	+	H_2S	=	H_2	+	PtS	$\Delta H = -16.0$ kcal/mol
ΔH_f(kcal/mol)	0		−4.8		0		−20.8	
	K_2O	+	H_2S	=	H_2O	+	K_2S	$\Delta H = -66.6$ kcal/mol.
ΔH_f(kcal/mol)	−86.4		−4.8		−57.8		−100	

CONCLUSIONS

1. The role of the Pt^{n+} ions in the Pt/KL zeolites, as catalysts for aromatization of n-C_6, was not established, possibly because of the effect of the retained hydrogen had obscured the results.

2. The presence of K^+ in the catalysts promotes aromatization of n-C_6.

3. Aromatization is more sensitive to sulfur in the presence of K^+.

4. Dehydrogenation is less sensitive to sulfur in the presence of K^+. Sulfur tolerance of Pt/KL for dehydrogenation is higher than that of the K^+-free Pt/SiO_2 catalysts.

5. K^+ interacts with sulfur more strongly than Pt and for this reason loses its ability to promote aromatization.

6. K^+ could be responsible for both the high aromatization activity and the high sulfur sensitivity of Pt/KL.

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