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A Novel Method in Preparation of Pt/KL Catalyst for Aromatization of Hexane

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It has been found that the addition of KCl to the Pt/KL catalyst prepared by ion exchange greatly improves the catalytic activity and selectivity for benzene formation. At the Cl/Pt molar ratio of 3.3, 99.8% conversion of hexane is obtained with an 88.3% yield of benzene.

Since Pt/KL was found to be a highly active and selective catalyst for the aromatization of hexane,1) a variety of modified methods have been applied to improve its catalytic properties.2,3) It has been proved that the treatment of KL zeolite with CF_3Cl prior to its impregnation with $[Pt(NH_3)_4]Cl_2$ results in enhanced activity and selectivity for hexane aromatization and stabilization of the catalytic performance.4) Poeppelmeier *et al.*5) have claimed in a patent that coimpregnation of KL zeolite with a solution containing $[Pt(NH_3)_4]Cl_2$ and KCl leads to an increase in selectivity for benzene. Quite recently, Sachtler *et al.*6) have compared the properties of Pt/KL catalysts prepared by ion exchange (IE), incipient wetness impregnation (IWI), and coimpregnation with KCl (IWI+KCl) employing various techniques, and have pointed out the IWI and IWI+KCl catalysts are less acidic, less active for hexane conversion, and more selective for benzene formation than the IE catalyst.

Here we report a novel and successful method in preparation of Pt/KL catalyst for hexane aromatization; Pt/KL catalysts prepared by ion exchange followed by impregnation with KCl give much higher activity and selectivity for benzene formation than the catalyst prepared by coimpregnation of KL zeolite with $[Pt(NH_3)_4]Cl_2$ and KCl.

The IE catalyst was prepared by ion exchange of KL zeolite (supplied from Tosoh) with an aqueous solution of $[Pt(NH_3)_4]Cl_2$. After stirring for 2 h at 343-353 K, the slurry was filtered and thoroughly washed with distilled water until chlorine was no longer detected. After drying at 393 K overnight, the Pt/KL catalyst was impregnated with KCl, dried again and then air-calcined at 573 K for 2 h. For the IWI catalyst, platinum was introduced into the KL zeolite by incipient wetness impregnation with an aqueous solution of $[Pt(NH_3)_4]Cl_2$. The catalyst was dried and calcined as described above for the IE catalyst. The IWI+KCl catalyst was prepared in a similar manner with the exception that the impregnating solution contained KCl. The catalysts were treated in flowing He at 393 K for 1 h and then reduced *in situ* in flowing H_2 at 773 K for 0.5 h. The reaction of hexane was carried out using a flow reactor made of a stainless-steel tube. Chlorine was extracted from the catalyst with boiling water and subjected to analysis by ion chromatography.

The catalytic performances of the 0.5 wt% Pt/KL catalysts for aromatization of hexane are illustrated in Table 1. Clearly, the activity and selectivity of the Pt/KL catalysts depended upon the preparation methods. The conversion of hexane on the IE catalyst was considerably high. Because of the hydrocracking occurring easily, however, the selectivity for benzene formation was not so high. The addition of KCl into the IE catalyst increased not only the hexane conversion but also the benzene yield. The large increase in the selectivity for benzene formation was accompanied with the decrease in that for hydrocracking and hydroisomerization.

On the IWI and IWI+KCl catalysts, both the activity and selectivity for benzene formation and hydrocracking were lower, and those for hydroisomerization were higher than on the IE catalyst. This is partly different from the results obtained by Sachtler *et al.*,6) who observed that the IWI and IWI+KCl catalysts were less selective for hydrocracking and more selective for benzene formation than the IE sample. They assumed that the protonic sites formed in the hydrogen reduction of Pt ions reacted with KCl as follows:

$$\text{Z-O}^{-}\text{H}^{+} + \text{KCl} \longrightarrow \text{Z-O}^{-}\text{K}^{+} + \text{HCl} \qquad (1)$$

It was speculated that this reaction concomitant with eventual escape of HCl resulted in decreased acidity. However, because there observed no virtual decrease in the Cl content after calcination and reduction (Table 2), the above reaction hardly occurred. Even if this reaction proceeded, such dramatic effect as was observed with the IE+KCl was not produced; it has been found neutralizing the protons with K_2CO_3 resulted in only a slight increase in the benzene yield.7)

Especially, the marked differences in the catalytic behavior between the IE+KCl and IWI or IWI+KCl catalysts are of interest. With the quite similar composition for the catalysts, the samples prepared by the addition of KCl to the ion exchanged Pt/KL catalyst (IE+KCl) gave much higher hexane conversion and benzene yield than the catalysts prepared by impregnation of KL zeolite with platinum (IWI) or coimpregnation of KL zeolite with platinum and KCl (IWI+KCl). With the IE+KCl (Cl/Pt=3.3) catalyst, the hexane conversion and benzene yield were as high as 99.8% and 88.3%, respectively, under the reaction pressure of 0.3 MPa; besides, the activity and selectivity of the catalyst remained unchanged over a reaction period up to 30 h.

Table 1. Comparison of Pt/KL Catalysts Prepared by Ion Exchange and Incipient Wetness Impregnation Methods [a)]

Catalyst	Method of preparation	Cl/Pt (molar ratio)	Conv. %	Yield/% Benzene	i-C6 [b)]	C1-C5	MCP	Benzene selectivity
Pt/KL	IE	0.0	96.9	63.2	11.5	20.3	0.9	65.2
KCl/Pt/KL	IE+KCl	1.5	97.6	76.2	8.7	11.3	0.7	78.1
KCl/Pt/KL	IE+KCl	3.3	98.3	77.4	6.7	13.1	0.5	78.7
KCl/Pt/KL [c)]	IE+KCl	3.3	99.8	88.3	0.8	10.3	0.1	88.4
Pt/KL	IWI	2.0	79.7	45.3	22.5	7.2	2.9	56.9
(KCl+Pt)/KL	IWI+KCl	3.8	72.4	38.8	22.0	6.6	3.3	53.6

a) Reaction conditions: pressure = 0.5 MPa, temperature = 743 K, WHSV = 2.4 h^{-1}, H2/hexane (molar ratio) = 6.0, time on stream = 3 h. b) 2-Methylpentane and 3-methylpentane. c) Pressure = 0.3 MPa.

Table 2. Analysis of Chlorine Content

Catalyst	Method of preparation	Cl/Pt (molar ratio)	Cl Content/μmol g-cat^{-1} After drying	After reduction	ΔCl [a)]
KCl/Pt/KL	IE+KCl	3.3	86.2	83.7	2.5
(KCl+Pt)/KL	IWI+KCl	3.8	99.2	98.3	0.9

a) The decrease in the Cl content assuming Eq.1 was estimated at 51.3μmol g-cat^{-1}.

It is generally recognized that the Pt/KL catalysts are monofunctional, having only a metal (platinum) function.[1-3,8)] A small amount of acidity is enough to decrease the hexane conversion into benzene, which increases with the zeolite basicity. The data shown in Table 3 indicates that for the IE+KCl catalysts the amount of adsorbed NH_3 decreased with the increase in the KCl content. The increased activity and selectivity for benzene production found with the IE+KCl catalysts may be partly attributed to the decreased acidity. However, perusal of the data in Table 3 shows that there is no clear correlation between the acidity and the catalytic behavior of the catalysts prepared in different ways.

As can be also seen in Table 3, the platinum dispersion was dependent upon the method of platinum loading, the values of the IE catalysts being slightly lower than those of the IWI catalysts at the similar Cl/Pt level. The TOF values of the IE+KCl catalysts increased by about 50% as compared with that of the IE catalyst with no KCl added, while the IWI and IWI+KCl catalysts exhibited lower activities. If we assume that

Table 3. Comparison of NH3 and H2 Chemisorption of Pt/KL Catalysts

Catalyst	Method of preparation	Cl/Pt (molar ratio)	NH3 mmol g-cat^{-1}	H/Pt	TOF s^{-1}
Pt/KL	IE	0.0	0.22	0.98	0.20
KCl/Pt/KL	IE+KCl	1.5	0.17	0.75	0.31
KCl/Pt/KL	IE+KCl	3.3	0.15	0.72	0.33
Pt/KL	IWI	2.0	0.21	1.03	0.13
(KCl+Pt)/KL	IWI+KCl	3.8	0.19	0.94	0.13

the platinum particles are spherical and the H/Pt$_{surface}$ equals 1, the average diameter of the platinum on the IE+KCl catalysts can be estimated to be *ca.* 1.5 nm. On the other hand, the size of Pt particles on the IWI catalysts is 1.1 nm or smaller. These findings are in agreement with those obtained by Besoukhanova *et al.*,3) who attributed aromatization activity to Pt particles of 1 to 2.5 nm and claimed the smaller ones to be inactive. The catalytic performances of the Pt/KL catalysts should be also affected by the location of the Pt particles, particle morphology, the electronic state of platinum,8) etc. The reasons for the enhancement of benzene production by the addition of KCl to the IE catalyst are not clear now and currently under study.

The effects of NH_4Cl and KNO_3 as additives to the IE catalyst have also been investigated. The activity increased with the addition of NH_4Cl, but practically unchanged in the case of KNO_3, suggesting that Cl rather than K is considered to be effective in the enhancement of the benzene production with the IE+KCl catalyst.

The present study has revealed the addition of KCl to the Pt/KL catalyst prepared by ion exchange as a novel and effective method for producing highly active catalysts for benzene formation from hexane.

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