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Effect of KCl Addition Method on the Pt/KL Catalyst for the Aromatization of Hexane

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The influence of the method for loading platinum precursor and adding KCl, KCl loading content, calcination temperature, KCl addition procedure, various additives, and water washing on the activity and selectivity of Pt/KL catalysts for hexane reforming reaction has been investigated. The catalyst preparation methods involve ion exchange (IE), incipient wetness impregnation (IWI), and coimpregnation with KCl (IWI–KCl). The Pt/KL catalysts prepared by ion exchange with $[Pt(NH_3)_4]Cl_2$ followed by impregnation with KCl (IE–KCl) gave much higher activity and selectivity for benzene formation than the catalysts prepared by coimpregnation of KL zeolite with $[Pt(NH_3)_4]Cl_2$ and KCl. The IE–KCl catalyst with KCl/Pt molar ratio of 4.5 showed 100.0% conversion of hexane and 89.3% yield of benzene at 743 K and 0.2 MPa. The IE–KCl catalysts exhibited lower H/Pt ratios than the IE catalyst. The KCl addition procedures markedly affected the activity and selectivity of the Pt/KL catalyst; the addition of KCl to the IE sample prior to calcination and reduction was necessary for the catalyst to exhibit the high activity in benzene formation. It has also been found that the performance of Pt/KL catalysts is markedly affected by the calcination temperature. With the IE–KCl catalysts, however, the decrease in the benzene yield caused by high-temperature calcination was not as serious as with the IE catalyst. In contrast, with the IWI and IWI–KCl catalysts, the activity for benzene production was highly sensitive to the calcination at high temperature, drastically decreasing by calcination at 823 K. The Cl species on the IE–KCl catalysts may have existed in the state of KCl.

INTRODUCTION

Catalytic reforming of naphtha typically transforms C_6–C_{10} straight-chain paraffins into aromatics and branched paraffins, increasing the octane number of the gasoline range hydrocarbons. Typical conventional reforming catalysts, noble metal clusters supported on an acidic carrier such as chlorinated alumina, have been used industrially to transform heavy naphtha into aromatics. In the classical scheme of the bifunctional catalysis proposed by Mills *et al.* (1), the cyclization occurs involving the metallic sites and the acidic sites of the chlorinated Al_2O_3. The paraffin is first dehydrogenated on the metal surface giving the corresponding olefin. This is protonated on the acidic site to give the carbonium ion, which undergoes cyclization followed by dehydrogenation. However, these catalysts show poor selectivities for aromatization of C_6 and C_7 paraffins (2), limiting, therefore, utilization of light napatha as a reforming feedstock.

Since platinum supported on KL zeolite was found to be a highly active and selective catalyst for the aromatization of hexane (3), numerous investigations have been carried out over the past decade in order to investigate two major characteristics of this novel zeolite catalyst.

First, particular attention has been focused on the explanations for the effectiveness of this catalyst with respect to the geometry of the zeolite support and the electronic state and morphology of the platinum particles. The majority of the studies have attributed the excellent and unique catalytic behavior of this catalyst to the unidimensional channel structure of KL, and several models to describe the process for benzene formation have been proposed (4–6). Derouane and Vanderveken suggest that the van der Waals interactions of hexane with the zeolite walls will preorganize the hydrocarbon in a pseudocycle prior to dehydrogenation (4). Because of the nonacidic nature of the KL zeolite, the Pt/KL catalyst was regarded as monofunctional rather than bifunctional (3, 7, 8), and the high activity and selectivity of the Pt/KL catalyst for the aromatization of hexane was viewed to depend only upon the Pt clusters, while the acidic sites of the support led to a decrease in activity and selectivity because of cracking/coking side reactions. The unique features of the Pt/KL catalyst were also ascribed to an interaction between the metal particles and the zeolite support. On the basis of infrared spectroscopic observations of adsorbed CO and competitive hydrogenation of benzene and toluene (8, 9), it has been shown that the properties of Pt particles are strongly dependent upon the surrounding zeolite structure and field, and that the Pt particles may be electron rich as a consequence of a charge transfer from the KL zeolite to the small metal particles.

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Second, in order to improve the catalytic properties, a variety of modified methods of synthesis have been investigated. In particular, the influence of varying zeolite acidity on the catalytic performance of Pt/KL catalyst has been investigated by several groups. It was observed that the activity and selectivity of Pt/KL catalyst were increased with decreasing the zeolite acidic sites by exchange with alkali or alkali earth cations (7–10). Our group has demonstrated that neutralization of the protonic sites formed in the hydrogen reduction of Pt ions with an aqueous solution of K_2CO_3 results in a sizable increase in the benzene yield (11). The effect of chlorine treatment on the properties of platinum supported on KL zeolite was studied by Foger and Jaeger (12). They found that agglomerated platinum on the zeolite catalysts was redispersed successfully by treatment with chlorine in nitrogen. A similar effect of chlorine-containing reagents was reported by Sugimoto and co-workers (13, 14), who observed 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, owing to improved dispersion of platinum particles. Poeppelmeier *et al.* (15) demonstrated that coimpregnation of KL zeolite with a solution containing $[Pt(NH_3)_4]Cl_2$ and KCl led to an increase in selectivity for benzene and dramatic improvement in catalyst deactivation. Quite recently, Sachtler and co-workers (16) have compared the properties of Pt/KL catalysts prepared by ion exchange (IE), incipient wetness impregnation (IWI), and coimpregnation with KCl (IWI–KCl) by employing various techniques, and have pointed out that the IWI and IWI–KCl catalysts are less acidic and less active for hexane conversion, and more selective for benzene formation than the IE catalyst.

In an earlier paper the present authors reported a novel method for preparing Pt/KL catalyst for aromatization of hexane, which resulted in high activity and selectivity for benzene formation (17). The purposes of this work are (i) to investigate the change in catalytic activity, selectivity, and stability for the aromatization of hexane when various alkali metal salts are added to the Pt/KL catalyst, (ii) to compare the effects of method for loading platinum and KCl on catalytic performance, (iii) to examine the effects of calcination temperature on the catalytic behavior of the Pt/KL catalysts prepared by different methods, and (iv) to study what effect removal of additives with water deposited on the reduced Pt/KL catalyst has on the Pt/KL catalysts.

EXPERIMENTAL

Catalyst Preparation

Zeolite-supported platinum catalysts, with a level of 0.50 wt.% of Pt loading, were prepared by ion exchange or impregnation method. Unless otherwise indicated, all catalysts were prepared by the following methods. To a stirred suspension of 50 g KL zeolite powder (supplied from Tosoh) in 1000 ml of distilled water was added 130 ml water containing 0.4293 g of $[Pt(NH_3)_4]Cl_2$ dropwise at about 350 K. After stirring for 2 h, the slurry was filtered and thoroughly washed with distilled water until Cl^- was no longer detected. The sample dried at 393 K overnight was designated as the IE catalyst. The IE sample was impregnated (0.57 ml H_2O: 1 g catalyst powder) with *MX* (*MX* = KCl, RbCl, KNO_3, K_2CO_3, or NH_4Cl) to incipient wetness and dried again. The catalysts thus prepared were called IE–*MX*. For the IWI catalyst, platinum was introduced into 30 g of the KL zeolite by incipient wetness impregnation with 17.1 ml water containing 0.2581 g $[Pt(NH_3)_4]Cl_2$. The IWI–KCl catalyst was prepared in a similar manner except that the impregnating solution contained additional KCl (KCl/Pt = 2.0). Unless otherwise noted, the catalysts were calcined in air at 573 K for 2 h. The calcined catalysts were pressed, crushed, and sieved in the range 20–40 mesh. The Pt loadings of the catalysts were determined by means of a ICAP-575 MarkII inductively coupled plasma (ICP) spectrometer and were found to be 0.44 wt.% for the IE series catalysts and 0.50 wt.% for the IWI series samples, respectively. Chloride deposited on the catalyst was extracted from the catalyst with boiling water and subjected to analysis by ion chromatography. The K concentration in washings was analyzed by atomic absorption spectroscopy.

Catalytic Reaction

All reactions for the conversion of hexane were carried out in a conventional continuous flow, fixed-bed type microreactor made of a stainless-steel tube 7.5 mm in diameter. In each run, 1 g dried catalyst sample was filled between quartz wool plugs held on stainless-steel spacers at the midpoint of the reactor. Prior to the reaction, the catalyst was purged in flowing helium at 393 K for 1 h at atmospheric pressure. Thereafter, the catalyst was reduced *in situ* in 0.5 MPa flowing 100% high-purity hydrogen at a flow rate of 100 ml/min/g catalyst by ramping the temperature from 393 to 773 K stepwise (100 K in 0.5 h), and then holding at the final temperature for 0.5 h. Hydrogen was purified by passage through a Deoxo unit followed by a 5 A molecular sieve gas drier. Liquid hexane was pumped into the reactor system at a rate of 2.4 g/h. The feed, gasified by the preheater at the top of the reactor, was carried by hydrogen to be passed through the catalyst bed.

The standard experimental conditions were as follows: reaction temperature of 743 K, total reaction pressure of 0.5 MPa, weight hourly space velocity of 2.4 h^{-1}, and a hydrogen-to-hexane molar ratio of 6.0.

The products were analyzed by an off-line FID gas chromatograph equipped with a 50-m OV-1 capillary column. Unless otherwise noted, the data were obtained after 3.0 h on stream.

H_2 Chemisorption

Platinum metal dispersion measurements by volumetric hydrogen chemisorption were carried out in a conventional glass vacuum system at room temperature. Catalyst (0.5 g) was outgassed at room temperature in vacuum and then pretreated in flowing He. The temperature was raised to 373 K at a heating rate of 6 K/min and held at 373 K for 0.5 h. The catalyst was then reduced in flowing H_2 while the temperature was raised from 373 to 773 K at a rate of 6 K/min and held at 773 K for 0.5 h. After reduction, the sample was evacuated ($<10^{-4}$ Torr) at 773 K for 1 h, cooled to room temperature in vacuum, and then the isotherms were recorded. The total amount of chemisorbed H atoms was obtained by extrapolating the linear higher pressure part of the isotherm to zero pressure. The platinum dispersion was conventionally defined as the ratio of the chemisorbed H atoms to the loaded platinum atoms.

RESULTS AND DISCUSSION

Effect of Method for Loading Pt and Adding KCl

Table 1 compares the results of the aromatization of hexane over the catalysts prepared by different methods. The catalysts were calcined at 573 K and then reduced in H_2 at 773 K. Clearly, there are significant differences between these catalysts, the activities and selectivities of the Pt/KL catalysts depending upon the preparation methods. The conversion of hexane on the IE catalyst was considerably high. Because of significant hydrocracking, however, the selectivity for benzene formation was not so high. The addition of KCl to the IE catalyst resulted in the increase in the benzene yield with a slight increase in the hexane conversion.

The considerable differences in the catalytic behavior between the IE-KCl (KCl/Pt = 2.3 or 4.5) and IWI (KCl/Pt = 2.0) or IWI–KCl (KCl/Pt = 4.0) catalysts are of interest. On the IWI and IWI–KCl catalysts, both the activities and selectivities for benzene formation and hydrocracking were lower, and those for hydroisomerization were higher than on the IE catalyst. However, although they had the approximately same composition of 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 catalyst prepared by impregnation of KL zeolite with platinum (IWI) or coimpregnation of KL zeolite with platinum and KCl (IWI–KCl). The IE–KCl (KCl/Pt = 4.5) catalyst exhibited the highest hexane conversion and benzene yield as high as 100.0% and 89.3%, respectively, under the reaction pressure of 0.2 MPa. In addition, the activity and selectivity of this catalyst remained unchanged over a reaction period up to 30 h. These results indicate that variations in the method for loading platinum and adding KCl resulted in marked differences in the performance of the catalysts for the aromatization of hexane.

In general, these Pt/KL catalysts should be compared at the same conversion levels since the benzene selectivity is known to increase monotonically with hexane conversion (18, 19). Hence the catalytic performance for the IE and IE–KCl catalysts at about 80% conversion obtained

TABLE 1

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

Catalyst	KCl/Pt[b] (molar ratio)	WHSV (h^{-1})	Conv. (%)	Selectivity (%)					Benzene yield (%)
				Benzene	*i*-C6[c]	C1–C5	MCP	Others[d]	
IE	0.0	2.4	96.9	65.2	11.9	20.9	1.0	1.0	63.2
IE	0.0	8.0	81.4	52.4	24.3	18.6	3.0	1.7	42.7
IE–KCl	2.3	2.4	97.8	75.7	8.0	15.0	0.6	0.7	74.0
IE–KCl	4.5	2.4	98.3	78.7	6.8	13.3	0.5	0.7	77.4
IE–KCl	4.5	12.0	79.5	62.1	25.0	8.2	3.1	1.6	49.3
IE–KCl[e]	4.5	2.4	100.0	89.3	0.4	10.0	0.0	0.3	89.3
IWI	2.0[f]	2.4	79.7	56.9	28.2	9.0	3.6	2.3	45.3
IWI–KCl	4.0[g]	2.4	72.4	53.6	30.4	9.1	4.6	2.3	38.8

[a] Catalysts were calcined at 573 K; standard reaction conditions: temperature = 743 K, pressure = 0.5 MPa, H_2/hexane = 6.0, WHSV = 2.4 h^{-1}, time on stream = 3 h.

[b] Molar ratio of added KCl to loaded Pt.

[c] 2-Methylpentane and 3-methylpentane.

[d] Mostly hexenes.

[e] Pressure = 0.2 MPa, time on stream = 5 h.

[f] KCl supposed to be generated by ion exchange, no KCl externally added.

[g] KCl supposed to be generated by ion exchange plus additional 2 moles of KCl introduced.

with varying reaction contact time is also shown in Table 1. The benzene selectivities observed over various catalysts were in the order IE–KCl > IWI > IWI–KCL > IE. The lower benzene selectivity for the IE catalyst was attributed to the higher C_1–C_5 selectivity. In contrast, the IE–KCl, IWI, and IWI–KCl catalysts exhibited lower C_1–C_5 selectivities. The results obtained with the IWI and IWI–KCl catalysts are quite similar to those found by Sachtler and co-workers (16). The IE–KCl and IWI (or IWI–KCl) catalysts were slightly different in their selectivities to hydroisomerization products. It is particularly noteworthy that in terms of the activity based on catalyst weight, the former was five times as high as the latter.

Our results are partly not in agreement with earlier reports (3, 16), which demonstrated that IWI or IWI–KCl preparations perform better than IE recipes for hexane aromatization reaction. Two plausible explanations exist for this difference in activity and selectivity as a function of preparation method. One is that our reaction conditions are far from those under which the catalytic properties of IE and IWI (or IWI–KCl) Pt/KL catalysts were compared, with regard to both temperature and pressure of reaction and H_2/hexane molar ratio (3, 16). In fact, the behavior differences between the IE and IWI catalysts were not so clearly visible under certain conditions, as shown in Bernard's report (3). Another explanation, as will be discussed later, is that the calcination temperature exerted a great influence on the catalytic properties. For example, we found that when calcined at 393 K, the IWI catalyst performed better than the IE catalyst.

Evidently, the above results are actually consistent with the observation that the residual acidity of the IE catalyst led to a lower selectivity for benzene formation because of the side reaction of cracking (3, 16). In the case of the IWI catalyst, relatively fast hydroisomerization, via 1–5 ring closure and subsequent ring opening, might result in retardation of 1–6 ring dehydrocyclization and subsequent dehydrogenation to produce benzene.

Sachtler and co-workers (16) also pointed out that the protonic sites formed in the reduction of Pt ions reacted with KCl as follows:

$$\text{Z-O}^-\text{-H}^+ + \text{KCl} \rightarrow \text{Z-O}^-\text{-K}^+ + \text{HCl}. \qquad [1]$$

It had been reported that this reaction associated with the eventual escape of HCl resulted in decreased acidity. With 0.44 (IE series) and 0.50 (IWI series) wt.% of Pt loadings, 45 and 51 μmol/g catalyst of proton should be present, since two protons will be formed from Pt^{2+} ions in the reduction process. Assuming completion of Eq. [1], the decrease in the Cl content was estimated to be 45–51 μmol/g catalyst. However, because, as we have observed, the Cl content remained virtually unchanged after calcination and reduction (Table 2), the above reaction appears to proceed only to a small extent in our catalyst preparation. Even if this reaction occurred extensively, such a dramatic effect as was observed with the IE–KCl was not produced; it has been found that neutralization of the protons with K_2CO_3 resulted in only a slight increase in the benzene yield (11). It should be mentioned that the loss of Cl content from the catalyst will depend on the preparation and reaction conditions, such as the calcination temperature, gas velocity, and position in the catalyst bed. In fact, about 20% decrease in the Cl content was observed when the IE–KCl catalyst was calcined at 823 K and then reduced at 773 K. Therefore, it is possible that the KCl reacted with the zeolite bulk or surface on certain conditions. It has been already found that agglomerated platinum on the L zeolite was redispersed successfully by treatment with chlorine (12) or with chlorine-containing reagents (13, 14). Studies on the role of Cl in the IE–KCl catalyst preparations and the relationship between the Cl content and the catalytic performance are currently in progress.

TABLE 2

Analysis of Chlorine Content

Catalyst	MCl/Pt (molar ratio) as impregnated[a]	Cl/Pt (molar ratio) after reduction[b]
IE–KCl	4.5	4.4 (3[c])
IWI–KCl	4.0[d]	4.0 (1[c])
IE–NH_4Cl	4.5	1.3 (72[c])

[a] Molar ratio of added *M*Cl (*M* = K^+ or NH_4^+) to loaded Pt.

[b] Residual Cl on the catalyst calcined at 573 K and followed by reduction at 773 K.

[c] Decrease in the Cl content by calcination and reduction (μ mol/g catalyst).

[d] KCl supposed to be generated by ion exchange plus additional 2 moles of KCl introduced.

Effect of KCl Loading Content

The influence of the added KCl content on the catalytic performance of the IE series catalysts for the aromatization of hexane has been investigated. As shown in Fig. 1, no effect of KCl was seen for KCl/Pt molar ratio of 1.1. The selectivity for benzene formation initially increased with added KCl, and a maximum yield of benzene was attained at a KCl/Pt ratio of 4.5, where the selectivity for hydrocracking and hydroisomerization products was minimized. With further addition the selectivity for benzene formation decreased slightly.

On reforming catalyst the formation or methane or pentane can be attributed to metallic sites (Hydrogenolysis) and that of propane to the acidic sites (acidic cracking) (20). Therefore, the changes of the ratios of the product yields, for instance, C_1/C_3 and C_5/C_3, might be used to

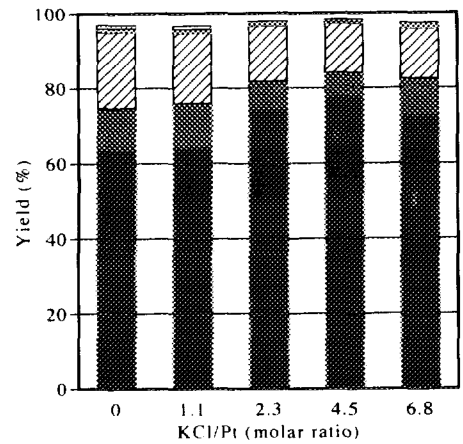

FIG. 1. Effect of KCl addition content on catalytic performance. (■) Benzene; (■) *i*-C6; (▨) C1–C5; (▦) MCP; (☐) others. Reaction conditions: see footnote to Table 1.

demonstrate which active site is affected by the KCl addition.

The changes of the molar ratio of C_1/C_3 and C_5/C_3 with the KCl addition are illustrated in Fig. 2. It was found that the ratio of hydrogenolysis to acidic cracking was increased with the addition of KCl to the IE catalyst. This means that the acidic cracking was suppressed by the KCl addition. Both the C_1/C_3 and C_5/C_3 molar ratios increased with increasing the amount of added KCl, reaching a maximum at KCl/Pt molar ratio of 4.5, and then slightly decreased with further increasing the KCl content. Thus these two ratios parallel the benzene selectivity.

The "terminal cracking index" (TCI), defined as the C_5/C_4 molar ratio in the cracking products, was proposed by Tauster and Steger (6). They found that the TCI increases paralleled the benzene selectivity. The C_5/C_4 molar ratios (TCI) for the catalysts are also plotted in Fig. 2. The TCI value similarly depends upon the KCl/Pt ratio, and correlates with the benzene selectivity, suggesting that the addition of KCl to the IE catalyst effectively promoted the probability of terminal adsorption of hexane at the platinum surface.

In line with the suppression of hydrocracking, the selectivity for hydroisomerization was decreased when KCl was added to the IE catalyst as shown in Fig. 1. Although such retarded hydrocracking and hydroisomerization was already observed with the Pt/KL catalysts prepared by the impregnation methods (3, 16), the IE-KCl catalyst produced a high conversion under the standard conditions, resulting in more selective formation of benzene.

Effect of Calcination Temperature

Figure 3 shows the yield of benzene under the standard reaction conditions as a function of calcination temperature for catalysts prepared by different methods. It can be seen that the IE-KCl series catalysts exhibited higher benzene yields than the IWI and IWI–KCl series catalysts when calcined at the same temperature. All catalysts calcined at 393 K gave the best results, except for the IE catalysts, which showed the highest benzene yield when calcined at 573 K. When calcined at 393 K, the IWI catalyst gave a higher benzene yield than the IE catalyst. A considerable decrease in the yield of benzene was observed when the calcination temperature was increased to 823 K for the IE catalyst. In the case of the IE–KCl catalysts, the yields of benzene remained virtually unchanged when calcined at 573 K; furthermore, the decrease in the benzene yield caused by high-temperature calcination (823 K) was not as serious as in the case of the IE catalyst.

In contrast to the IE and IE–KCl series catalysts, the IWI and IWI–KCl catalysts showed high sensitivity to the calcination temperature. The yields of benzene drastically

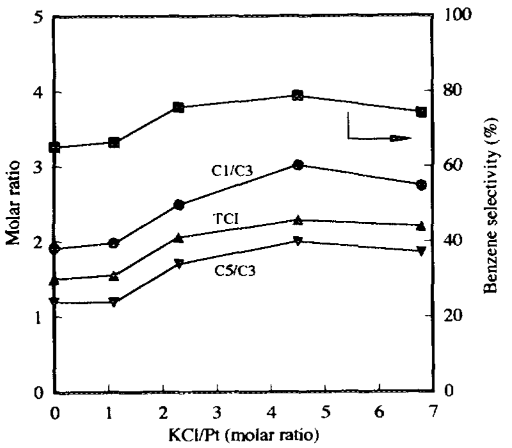

FIG. 2. Effect of KCl addition content on benzene selectivity and cracking parameter. Reaction conditions: see footnote to Table 1.

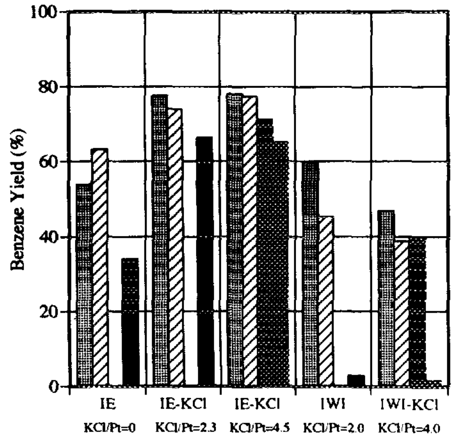

FIG. 3. Effect of calcination temperature and preparation methods on benzene yield over Pt/KL catalysts. (■) 823 K; (■) 673 K; (▨) 573 K; (▦) 393 K. Reaction conditions: see footnote to Table 1.

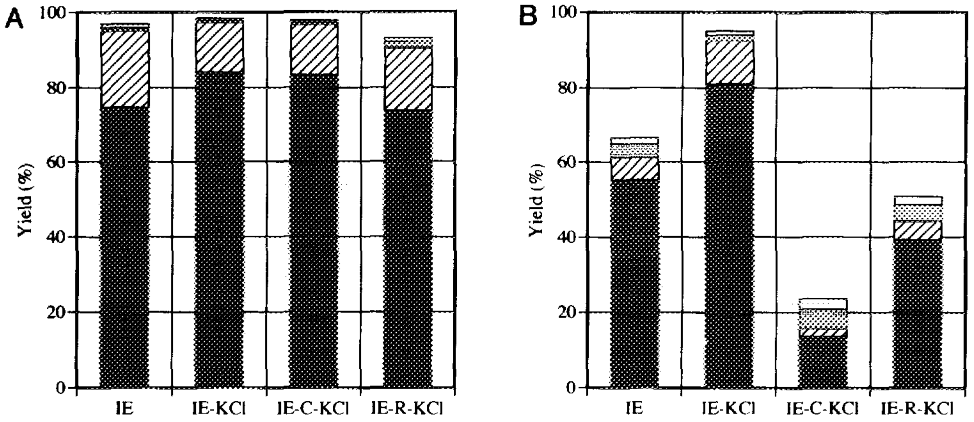

FIG. 4. Effect of KCl addition procedure on catalytic performance. (■) Benzene; (■) *i*-C6; (▨) C1–C5; (▦) MCP; (□) others. (A) Calcination temperature = 573 K; reduction temperature = 773 K. (B) Calcination temperature = 823 K; reduction temperature = 773 K. Reaction conditions: see footnote to Table 1.

decreased when these catalysts were calcined at 823 K. At the same calcination temperature, the yield of benzene with the IWI-KCl catalyst was slightly lower than that with the IWI catalyst.

The effect of calcination temperature on the activity and selectivity of Pt-zeolite catalyst has been investigated by several researchers (21–24). Reagan *et al.* (23) have studied the chemistry of thermal decomposition of the platinum ammine complex in NaY zeolite under H_2 or He. They observed that the calcination at 573 K led to a Pt/NaY catalyst showing the optimum activity in dehydrogenation and dehydrocyclization and that this temperature was necessary for the decomposition of the $[Pt(NH_3)_4]^{2+}$ complex to proceed within a reasonable time. The results of the IE catalyst, as shown in Fig. 3, are consistent with their observation. In the case of Pt/KL catalysts containing KCl (IE–KCl, IWI, and IWI–KCl), however, the calcination at 393 K resulted in the optimum activity and selectivity in the production of benzene. It is conceivable that in the presence of KCl the decomposition of the Pt ammine complex occurs at low temperatures. Infrared and temperature-programmed reduction measurements are being undertaken to clarify its decomposition behavior.

Effect of KCl Addition Procedure

Three kinds of catalysts were prepared according to different KCl addition procedures: KCl was added to the dried IE catalyst (IE–KCl), dried and calcined IE catalyst (IE–C–KCl), and dried, calcined, and reduced catalyst (IE–R–KCl). The product yields are presented in Figs. 4A and 4B, where the calcination temperatures were 573 and 823 K, respectively. The product distribution is shown in Table 3. The catalyst prepared according to the standard addition procedure, IE–KCl, exhibited the highest activity in benzene formation with both calcination temperatures. When calcined at 573 K, the IE–C–KCl was an improvement on the IE catalyst. However, the IE–R–KCl catalyst gave rise to a lower benzene yield than the IE catalyst; the addition of KCl after reduction affected the IE–R–KCl detrimentally. When calcined at 823 K, the IE–C–KCl and IE–R–KCl catalysts showed quite low activity compared with the IE or IE–KCl catalysts. These results indicate that the catalytic properties of the Pt/KL catalysts depend markedly on the KCl addition procedures, and that during decomposition of the $[Pt(NH_3)_4]^{2+}$ in the KL zeolite at high temperature the presence of KCl is vital to a high yield of benzene production.

Effect of MX (MX = KNO_3, K_2CO_3, NH_4Cl) Addition

By using KNO_3 or K_2CO_3 instead of KCl, catalysts were prepared in a similar way to IE–KCl. The catalysts were calcined at 573 K. As shown in Fig. 5 and Table 4, the

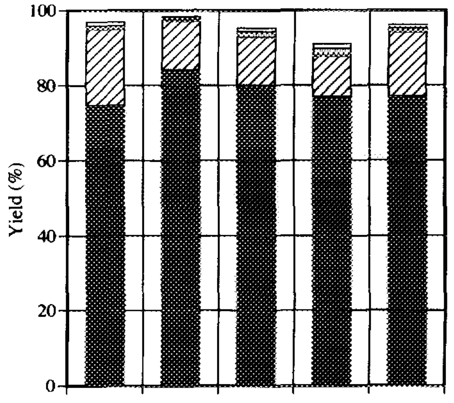

FIG. 5. Effect of different additives on catalytic performance. (■) Benzene; (■) *i*-C6; (▨) C1–C5; (▦) MCP; (□) others. Reaction conditions: see footnote to Table 1.

TABLE 3

Effect of KCl Addition Procedure on Catalytic Performance[a]

Catalyst	KCl/Pt[b] (molar ratio)	Calc. temp. (K)	Conv. (%)	Selectivity (%)					Benzene yield (%)
				Benzene	*i*-C6[c]	C1–C5	MCP	Others[d]	
IE	0.0	573	96.9	65.2	11.9	20.9	1.0	1.0	63.2
IE–KCl	4.5	573	98.3	78.7	6.8	13.3	0.5	0.7	77.4
IE–C–KCl[e]	4.5	573	97.8	76.5	8.8	13.5	0.7	0.5	74.8
IE–R–KCl[f]	4.5	573	93.1	59.7	19.5	17.8	1.8	1.1	55.6
IE	0.0	823	66.4	51.2	32.1	8.7	5.6	2.4	34.0
IE–KCl	4.5	823	95.0	68.5	16.7	12.1	1.5	1.2	65.1
IE–C–KCl[e]	4.5	823	23.5	25.5	32.8	8.9	21.3	11.5	6.0
IE–R–KCl[f]	4.5	823	50.8	40.4	37.0	9.6	8.7	4.3	20.5

[a] Standard reaction conditions: see footnote to Table 1.

[b] Molar ratio of added KCl to loaded Pt.

[c] 2-Methylpentane and 3-methylpentane.

[d] Mostly hexenes.

[e] KCl was added to calcined IE sample.

[f] KCl was added to calcined IE sample and reduced at 773 K.

activity and selectivity for benzene formation remained practically unchanged in the case of KNO_3, but decreased with the addition of K_2CO_3. Thus, the Cl anion is regarded as playing a key role in increasing the yield of benzene formation.

Different from KCl, easily sublimable NH_4Cl is expected to be removed from the Pt/KL catalyst by calcination and following reduction. As shown in Table 2, only 30% of the added chlorine remained, Cl/Pt molar ratio being only 1.3. It therefore appears reasonable to imagine that the alkali metal cations function as a chlorine anchor. A slight difference in the catalytic performance was found between the IE–NH_4Cl and IE catalysts.

Effect of Water Washing

As described above, no significant decrease in the Cl content was observed after calcination at 573 K and reduction at 773 K for both IE–KCl and the IWI–KCl catalysts. In order to determine how such additives as KCl produced influences on the properties of Pt/KL catalysts, the effect of hot water washing to eliminate residual potassium chloride on the reduced IE–KCl catalyst was studied.

Table 5 shows the chlorine and potassium content in water extracts from the IE–KCl. It is shown that most of the chloride was removed from this catalyst by washing. The amount of K leached corresponded well to that of Cl leached, indicating that Cl was extracted as KCl. The results of the hexane reaction on the unwashed and washed catalysts are shown in Fig. 6 and Table 6. The activity and selectivity for benzene production decreased by washing. This indicates that Cl species must be present on the catalyst surface during the hexane aromatization reaction. The Cl species were easily soluble in hot water, where they were present in the state of KCl, and hence might have existed in the form of KCl on the catalyst

TABLE 4

Effect of Different Additives on Catalytic Performance[a]

Catalyst	*M*/Pt[b] (molar ratio)	Conv. (%)	Selectivity (%)					Benzene yield (%)
			Benzene	*i*-C6[c]	C1–C5	MCP	Others[d]	
IE	0.0	96.9	65.2	11.9	20.9	1.0	1.0	63.2
IE–KCl	4.5	98.3	78.7	6.8	13.3	0.5	0.7	77.4
IE–KNO_3	4.5	95.2	66.1	18.1	13.2	1.6	1.0	62.9
IE–K_2CO_3	4.5	91.0	60.8	23.8	11.8	2.2	1.4	55.3
IE–NH_4Cl	4.5	96.1	67.3	12.9	17.7	1.0	1.0	64.7

[a] Catalysts were calcined at 573 K; standard reaction conditions: see footnote to Table 1.

[b] Molar ratio of added M ($M = K^+$ or NH_4^+) to loaded Pt.

[c] 2-Methylpentane and 3-methylpentane.

[d] Mostly hexenes.

TABLE 5

Analysis of Potassium and Chlorine Present in Water Extracts

Catalyst	KCl[a] (μmol/g catalyst)	K[b] (μmol/g catalyst)	Cl[b] (μmol/g catalyst)
IE–KCl	103	91 ± 1	89 ± 1

[a] KCl added to the catalyst.

[b] K and Cl present in water extracts from the catalyst calcined at 573 K and followed by reduction at 773 K.

during the reaction. With the washed catalyst, acid-promoted side reactions such as hydrocracking and hydroisomerization could not be retarded enough, resulting in the decrease in the benzene yield.

As described above, KCl added after Pt reduction was harmful to the benzene production. KCl should be added before calcination, and it is evident that during the calcination and following the reduction KCl acted favorably for the formation of active species for benzene production. However, it is likely that after this process KCl remained as such and affected the benzene formation directly in the hexane aromatization reaction.

Pt Particle Dispersion

Several groups have reported that extremely small platinum particles incorporated within the pores of KL zeolite and stabilized in a nonacidic environment are ideal for hexane aromatization (19, 25–27). The effect of the KCl addition on the H/Pt ratio is summarized in Table 7. It is evident that the platinum dispersion depended upon the method and calcination temperature in the preparation of Pt/KL catalysts. For the IE catalyst without KCl, the H/Pt ratio increased slightly as the calcination temperature increased from 393 to 573 K, but decreased sharply with raising the calcination temperature to 823 K. A similar effect on the H/Pt ratios was observed with the calcination of the IE-KCl series catalysts. However, it is noticeable that the addition of KCl significantly suppressed the sintering of platinum when the catalysts were calcined at 823 K.

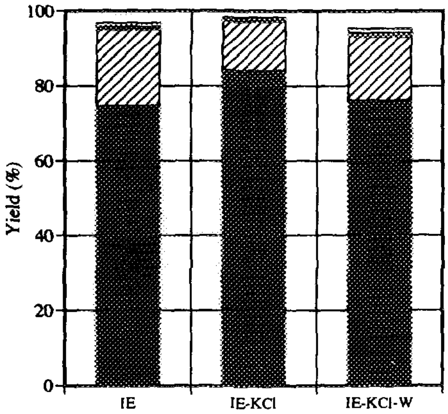

FIG. 6. Effect of water washing on catalytic performance. (■) Benzene; (■) *i*-C6; (▨) C1–C5; (▤) MCP; (□) others. Reaction conditions: see footnote to Table 1.

The H/Pt ratios of the IWI and IWI–KCl catalysts decreased with increasing the calcination temperature, suffering a sharp decline at 823 K, in particular. This means that the platinum dispersion of the IWI and IWI–KCl catalysts were highly sensitive to calcination temperatures higher than 673 K. It is also worth noting that there is a trend towards lower Pt dispersion with increased KCl loadings for the same series of Pt/KL catalysts, except for the IE and IE–KCl samples calcined at 823 K.

The changes in platinum dispersion with the calcination temperature are in good agreement with the hexane reaction results shown in Fig. 3 for the same series catalysts. The extremely low activity of the IWI and IWI–KCl catalysts calcined at 823 K in the benzene production could result from their very low H/Pt ratios. On the other hand, the preserved activity of the IE–KCl catalysts calcined at 823 K should be related to their relatively high H/Pt ratios. This indicates that the KCl addition method in preparation of Pt/KL catalyst exerts a great influence on the Pt particle stability during high-temperature calcination.

For the catalysts calcined at 393 or 573 K but prepared in different ways, there is no clear correlation between the platinum dispersion (Table 7) and the catalytic performance (Table 1, Fig. 3). For example, the activity on a weight basis of the IE–KCl samples in benzene formation was higher than that of the IE, IWI, and IWI–KCl samples, although the H/Pt values of the former were lower than those of the latter. The turnover frequencies (TOF (sec^{-1})) based on H_2 chemisorption site densities and benzene produced at conversions in the range 72–81% are also shown in Table 7. Surprisingly, although with the approximately same composition of the catalysts, the IE–KCl catalyst (KCl/Pt = 4.5) gave much higher TOF than the IWI–KCl catalyst (KCl/Pt = 4.0), the former being 7.3 times as high as the latter. Furthermore, although there was no significant difference in the H/Pt values among the IE, IWI, and IWI–KCl catalysts cal-

TABLE 6

Effect of Water Washing on Catalytic Performance[a]

Catalyst	KCl/Pt[b] (molar ratio)	Conv. (%)	Selectivity (%)					Benzene yield (%)
			Benzene	i-C6[c]	C1–C5	MCP	Others[d]	
IE	0.0	96.9	65.2	11.9	20.9	1.0	1.0	63.2
IE–KCl	4.5	98.3	78.7	6.8	13.3	0.5	0.7	77.4
IE–KCl–W[e]	0.0	95.4	65.1	14.8	17.8	1.2	1.1	62.1

[a] Catalysts were calcined at 573 K; standard reaction conditions: see footnote to Table 1.

[b] Molar ratio of added KCl to loaded Pt.

[c] 2-Methylpentane and 3-methylpentane.

[d] Mostly hexenes.

[e] KCl was removed from the IE–KCl (KCl/Pt = 4.5) sample by washing.

cined at 823 K, the IE sample gave a much higher benzene yield than the IWI and IWI–KCl catalysts. These findings indicate that the catalytic performance of hexane aromatization is affected not only by the platinum particle size in the zeolite catalyst but also by the location of the Pt particles, particle surface morphology, electronic state of platinum, etc. (9). In fact, based on the result of competitive hydrogenation reaction of benzene and toluene on Pt particles, we have found that the platinum particles on the IE–KCl (KCl/Pt = 4.5) catalyst are electron rich, while those on the IWI–KCl catalyst are electron deficient compared with those on the IE catalyst (28).

The IE–C–KCl and IE–R–KCl catalysts calcined at 823 K gave lower H/Pt ratios than the IE catalyst. These are in good agreement with the aromatization results shown in Fig. 4B. This indicates that low activities based on the weight of IE–C–KCl and IE–R–KCl catalysts calcined at 823 K might be mainly attributed to the growth of the Pt particles. However, the IE–C–KCl and IE–R–KCl calcined at 573 K showed moderately high H/Pt ratios. In these cases there is no clear correlation between H/Pt ratios and catalytic performances (Fig. 4 A). With Pt surface areas large enough, the activity might be affected by other factors besides Pt particle sizes as described above.

It may be assumed that once reduced, because of autoreduction by NH_3 or reduction by hydrogen (24), the platinum particles were no longer favorably affected by KCl. The addition of KCl to the IE sample calcined at 573 K and reduced at 773 K, with H/Pt ratio of 1.11, resulted in the decreased H/Pt ratio of 0.90; the platinum particles thus formed were slightly blocked or poisoned by the addition of KCl, giving rise to the decrease in the benzene yield.

TABLE 7

Hydrogen Chemisorption of Various Pt/KL Catalysts

Catalyst	KCl/Pt[a] (molar ratio)	H/Pt at various calcination temperatures				TOF[b] (sec^{-1})
		393 K	573 K	673 K	823 K	
IE	0.0	0.97	1.11	—	0.19	0.39
IE–KCl	1.1	—	1.01	—	—	—
IE–KCl	2.3	0.77	0.85	—	0.44	—
IE–KCl	4.5	0.77	0.82	0.73	0.53	0.92
IE–KCl	6.8	—	0.78	—	—	—
IWI	2.0[c]	1.13	1.03	—	0.22	0.14
IWI–KCl	4.0[d]	1.04	0.94	0.91	0.18	0.13
IE–C–KCl	4.5	—	0.77	—	0.07	—
IE–R–KCl	4.5	—	0.90	—	0.13	—

[a] Molar ratio of added KCl to loaded Pt.

[b] Benzene produced (metal site)$^{-1}$ · sec^{-1}; conversions in the range 72–81%; TOF determined at 743 K and 0.5 MPa, catalysts calcined at 573 K.

[c] KCl supposed to be generated by ion exchange.

[d] KCl supposed to be generated by ion exchange plus additional 2 moles of KCl introduced.

TABLE 8

Hydrogen Chemisorption of Various Pt/KL Catalysts[a]

Catalyst	M/Pt[b] (molar ratio)	H/Pt
IE	0.0	1.11
IE–KCl	4.5	0.82
IE–KNO_3	4.5	1.31
IE–K_2CO_3	4.5	1.22
IE–NH_4Cl	4.5	0.60

[a] Catalysts were calcined at 573 K.

[b] Molar ratio of added M (M = K^+ or NH_4^+) to loaded Pt.

In contrast to the addition of KCl, the addition of KNO_3 and K_2CO_3 resulted in high H/Pt values, compared with that of IE catalyst (Table 8). However, the activities and selectivities of these catalysts, as shown in Fig. 5, were not superior to those of the IE sample. Therefore, one may consider that the presence of potassium ion unaccompanied by chloride ion may result in inferior performance.

In the case of the IE–NH_4Cl catalyst, the platinum dispersion was only 0.60, being about half as much as that of the IE sample. It can be seen from Fig. 5, however, that the former exhibited a slightly higher activity and selectivity for benzene production than the latter. This result might be attributed to the beneficial effect of residual chlorine on the Pt/KL catalyst, compensating for the decrease in the platinum dispersion.

We also found that there was no significant difference in the H/Pt ratio between the IE–KCl and IE–KCl–W catalysts calcined at 573 K and reduced at 773 K. This suggests that the low H/Pt ratios of the IE–KCl catalysts compared with that of the IE sample were not due to a physical site blocking effect of KCl species. Thus the effect of KCl in the IE–KCl catalysts is different from that in the IE–R–KCl catalyst, where KCl blocked or poisoned platinum particles, resulting in the low H/Pt ratio compared to the IE sample. On the contrary, the decrease in the H/Pt ratio with the addition of KCl for the IE–KCl catalysts is probably ascribed to the increase in the platinum particle size. To reveal the location and size of the platinum particles, electron micrographic studies are now in progress.

CONCLUSIONS

The following conclusions emerge as a result of this study:

1. The activity and selectivity for benzene formation in the aromatization of hexane depend strongly upon the methods for loading platinum precursor, additives, addition procedures, and calcination temperature.
2. The IE–KCl catalyst, which is prepared by ion exchange followed by addition of KCl (KCl/Pt = 4.5) and subsequent calcination at 573 K, exhibits an optimum catalytic performance. This catalyst has a lower H/Pt ratio than the catalyst without KCl addition. The Cl anion plays a more essential role than the K cation in improving the Pt/KL catalytic properties.
3. KCl added to the ion exchanged (IE) catalyst prevents the platinum particles from sintering at high calcination temperature. In contrast, KCl added through impregnation together with Pt exhibits an adverse effect.
4. KCl must be present on the IE–KCl catalyst surface during the hexane aromatization reaction. KCl on this catalyst is effective in retarding hydrocracking and hydroisomerization, improving the benzene yield.

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