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Effect of halogen anion on hexane aromatization activity of Pt/KL catalysts

Takashi Tatsumi [1,2], Lian-Xin Dai [2] and Haru Sakashita

Department of Applied Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Tokyo 113, Japan

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Potassium salts were added to the catalyst prepared by ion exchange of KL with $[Pt(NH_3)_4]Cl_2$ and the effect of their counter anion on the activity and selectivity for hexane aromatization was studied. The catalyst to which KF was added showed the highest activity and selectivity for benzene formation; methylcyclopentane and hydroisomerization products were negligible. Although the catalyst with KCl added also exhibited excellent performance, the catalysts with KBr or KI added gave rise to low hexane conversion and benzene yield. Infrared spectra of adsorbed CO revealed that the presence of the low frequency C–O stretching band is closely related to catalytic performance of the Pt/KL series catalysts. The electron-rich Pt site formed through the interaction with KF or KCl may be responsible for the high activity and selectivity for hexane aromatization.

Keywords: Pt/KL zeolite; FT-IR spectroscopy; CO adsorption; halogen anion effect

1. Introduction

Non-acidic reforming catalysts based on Pt particles in L zeolite have been extensively studied during the past decade. It was shown that the acidic sites of the support not only did not take part in the reforming reaction but their presence caused a decrease in catalytic activity and selectivity because they promote cracking/coking side reactions [1–4]. The unique features of these catalysts have been ascribed to an interaction between metal particles and the zeolite support [1–7]. On the other hand, it has been suggested that the high aromatization performances of platinum supported on L zeolites results from the channel structures of zeolite [8–11]. Derouane and Vanderveken [8] claimed that the van der Waals interaction of the hydrocarbon with the channel walls led to preorganization of hexane as a pseudocycle. Tauster and Steger [9] proposed that the high aromatization selectivity of Pt

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[1] To whom correspondence should be addressed.

[2] Present address: Engineering Research Institute, Faculty of Engineering, The University of Tokyo, Yayoi, Tokyo 113, Japan.

supported in L zeolite was caused by the ability of the channels to collimate the diffusing flux of hexane molecules so that their long axes were parallel to the channel, leading to terminal adsorption on the Pt surface. Recently Mielczarski et al. [12] stated that uniqueness of Pt/KL catalysts for hexane aromatization lies not in the geometry of their channel structure but in the ability to stabilize extremely small Pt clusters in a non-alkali environment.

Much attention has been paid to studying the influence of alkali or alkali earth cations on the catalytic performance of Pt/L catalysts. The zeolite acidity/basicity is varied when the zeolite is exchanged with different cations [2–4,6,7,13,14]. Very recently, it has been reported that Ba cations deposited decreased aromatization reactivity by causing channel blocking [15]. Counter anions are introduced into the zeolite when platinum or alkali/alkali earth metal was loaded through impregnation of the zeolite. However, the effect of counter anions thus introduced on the hexane aromatization activity has been scarcely studied. We have already reported that potassium chloride acts as an effective additive to the Pt/KL catalyst prepared by ion exchange, giving rise to highly active and selective catalysts for hexane aromatization [16]. Here we report the remarkable effect of counter anion on the hexane aromatization activity of Pt/KL catalysts.

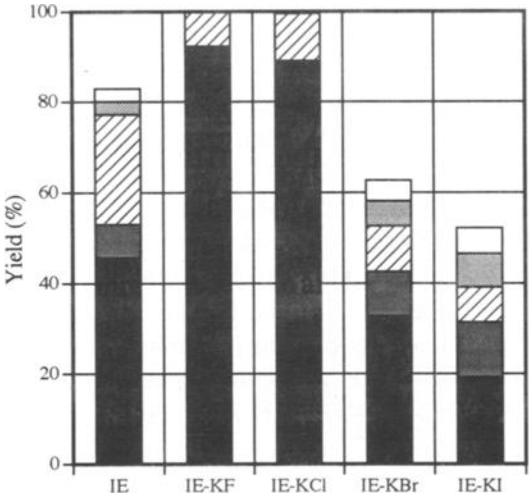
2. Experimental

Zeolite KL-supported Pt catalysts with 0.44 wt% loading were prepared by ion exchange of KL with $[Pt(NH_3)_4]Cl_2$, and designated as IE catalyst. The IE catalyst was impregnated with potassium halide salts KX (KX/Pt molar ratio = 4.5) to incipient wetness to afford IE-KX catalysts. After calcination in air at 573 K for 2 h, the catalysts were reduced in situ in flowing H_2 at 773 K for 0.5 h. The reaction of hexane was carried out using a conventional fixed-bed reactor. Typical experimental conditions were as follows: reaction temperature of 743 K, total pressure of 0.2 MPa, weight hourly space velocity (WHSV) of 2.4 h^{-1} and H_2 to hexane molar ratio of 6.0.

Hydrogen and ammonia chemisorption measurements were carried out at room temperature by using a conventional glass-made static vacuum system. The total amount of chemisorbed H atoms was obtained by extrapolating the linear part of the adsorption isotherms to the zero pressure. The amount of chemisorbed NH_3 was obtained by subtracting the two isotherms and extrapolating the results to zero pressures. Infrared spectra of adsorbed CO were taken on a Perkin-Elmer 1600 FT-IR instrument.

3. Results and discussion

The hexane aromatization performance of IE-KX (X = F, Cl, Br and I) catalysts are presented in fig. 1. The IE-KF catalyst showed the highest activity and



	IE	IE-KF	IE-KCl	IE-KBr	IE-KI
Conv.(%)	82.9	100.0	100.0	62.7	52.2
H/Pt	1.11	1.06	1.00	0.50	0.11

Fig. 1. Effect of addition of potassium halides on the catalytic performance. (■) Benzene; (■) i-C_6; (▨) C_1–C_5; (▤) MCP; (□) others.

selectivity for benzene formation; methylcyclopentane (MCP) and hydroisomerization products were negligible. Although the IE-KCl catalyst also exhibited excellent performance, the IE-KBr and IE-KI catalysts gave rise to low hexane conversion and benzene yield and thus the order of activity and selectivity for benzene production was IE-KF > IE-KCl > IE > IE-KBr > IE-KI. Neither K_2CO_3 nor KNO_3 added to the IE catalyst in a similar manner was found to affect the catalyst performance beneficially. No improvement over the IE catalyst was observed when KCl addition was performed after the reduction of Pt.

The H/Pt ratios of the Pt/KL catalysts are shown in fig. 1. It is clearly seen that for all the IE-KX catalysts, the H/Pt ratios were lower than that of the IE sample. Thus the enhancement of hexane conversion and benzene production by the addition of KF or KCl to the IE catalyst cannot be explained by the increase in the Pt dispersion. The H/Pt ratio decreased monotonously with increasing halogen atomic number. Except for the IE catalyst, the hexane conversion paralleled well with the Pt dispersion.

One might wonder that the low H/Pt ratio for the IE-KI sample is due to the bulkiness of I^- anion prohibiting the accessibility of the Pt particles deeply inside the zeolite crystals. The potassium halide salts were removable by washing the reduced catalyst with hot water. Removal of KI by washing the IE-KI catalyst with hot water, however, resulted in no change in the H/Pt ratio. Thus the low activity on a weight basis of the IE-KBr and IE-KI catalysts would be at least partly ascribable to the decrease in the Pt dispersion. Activity based on catalyst weight was estimated from 40–60% hexane conversion data obtained by varying the WHSV; the activity of the IE-KF and IE-KCl catalysts was about 4.5 times as high as that of the IE catalysts.

Infrared spectra of CO adsorbed on the IE and IE-KX series catalysts are shown in fig. 2. The main bands at 2070–1950 cm^{-1} are due to the linear-bonded CO and a second broader band located around 1780–1820 cm^{-1} due to bridge-bonded CO [2,5,17–19]. Only two bands were present on the IE, IE-KBr, and KI catalysts. Two additional CO adsorption bands assigned to linear-bonded CO were observed for the IE-KCl and IE-KF catalysts. One was higher and the other lower in wavenumber than the predominant band. For the IE-KF catalyst the lower wavenumber band was rather strong. The predominant bands shifted to lower frequency with decreasing atomic number of the halogen. The series of decreasing wavenumber was IE>IE-KI>IE-KBr>IE-KCl>IE-KF. The wavenumber of the bridge bands followed the same order. Since lower wavenumber indicates more electron-richness of the Pt particles, this order is in agreement with the high specific activity of the Pt particles on the IE-KF and IE-KCl catalysts. Besoukhanova et al. [2] reported that the position of CO absorbance was dependent on the cation (Li^+, K^+ or Rb^+) exchanged into the zeolite. However, the frequency shifts were relatively small compared to those observed with the IE-KX series catalysts.

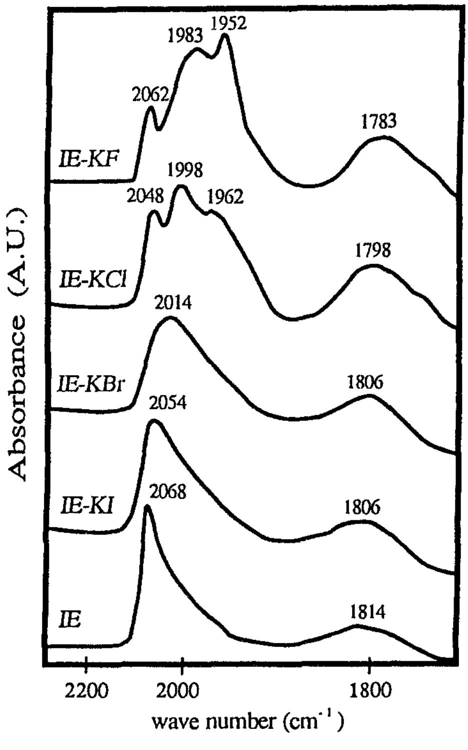


Fig. 2. FT-IR spectra of CO adsorbed on the various Pt/KL catalysts.

One might consider that the electron-richness of Pt particles on KF-modified catalyst contradicts the high electronegativity of F. The formation of a Pt–X bond can be excluded since a steady decrease in the C–O stretching frequency in Pt halogen carbonyl complexes was found to occur as the atomic number of the halogen was increased [20,21], reflecting the increasing importance of π-back donation from Pt to CO as the electronegativity of the halogen decreased.

It is conceivable that the potassium salts were present as such on the catalyst, since they were extractable with hot water as described above. The washed IE-KF and IE-KCl catalysts, whose H/Pt ratio remained unchanged, no longer exhibited the low frequency ν(CO) band around 1960–1950 cm^{-1} and gave lower activity in the benzene formation than the IE catalyst, being consistent with the lower H/Pt ratio. Thus it has been confirmed that the presence of the low frequency band is closely related to the catalytic performance of the Pt/KL series catalysts. The electron-rich Pt site formed through the interaction with KF or KCl may be responsible for the high activity and selectivity for hexane aromatization. The halogen anions F^- and Cl^- associated with K may donate electrons to the Pt particles. Mallmann and Barthomeuf [5] suggested that most active Pt atoms for hexane aromatization were the atoms activated by the negatively charged framework oxygen atoms and exhibiting lower frequency CO bands. In this regard it is also noteworthy that KF impregnated into Al_2O_3 exerted powerful basicity [22].

It has been proposed that the selectivity for aromatics increases with increasing electron-richness or decreasing electron deficiency of the platinum particles [1–7,23]. Davis and Derouane [24,25] reported that hexane aromatization selectivity on Pt/MgO is similar to that on Pt/KL and ruled out any effects of microporosity. They instead speculated on metal–support interactions between Pt clusters and a high surface area basic support; it has been claimed that the atomic and electronic structure of the Pt clusters are optimized through the interactions in such a way to demonstrate the high performance in benzene formation.

The two dominant reaction paths for hexane are 1–6-ring closure to form benzene and 1–5-ring closure to form MCP which is followed by ring opening to form 2- and 3-methylpentanes (MPs) [26]. Fig. 3 plots the product selectivity as a function of hexane conversion for the IE-KX catalysts. The conversion on the IE-KCl catalysts was changed by varying the WHSV at the temperature kept constant. Comparison of selectivities at the similar hexane conversion demonstrates that the IE-KCl and IE-KF catalysts offer significant selectivity advantages over the other catalysts. One might wonder the improved performances of these catalysts may be due to decreased acidity. The NH_3 adsorption data showed that the acidity of IE-KX catalyst was essentially independent of X and significantly lower than that of the IE catalyst, in agreement with the lower selectivity for hydrocracking. However, the study on the method of preparation of Pt/KL catalysts modified with KCl has revealed that there is no clear correlation between the acidity and the selectivity for benzene [27]. The IE-KX catalysts with similar acidities showed selectivities differences for aromatization and MCP/MPs formation.

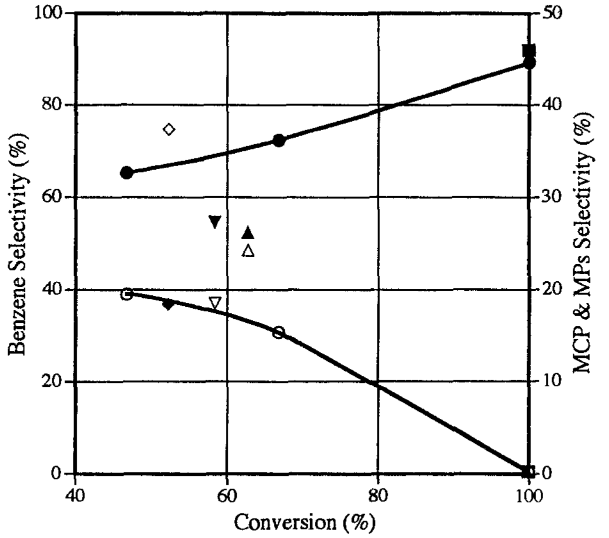


Fig. 3. Product selectivity as a function of hexane conversion for the various Pt/KL catalysts. Benzene selectivity: (■) IE-KF; (●) IE-KCl; (▲) IE-KBr; (◆) IE-KL; (▼) IE-KCl-W. MCP and MPs selectivity: (□) IE-KF; (○) IE-KCl; (△) IE-KBr; (◇) IE-KI; (▽) IE-KCl-W.

Tauster and Steger [9] proposed that high aromatization selectivity of Pt/KL compared to Pt/SiO$_2$ resulted from an enhanced probability of terminal adsorption of hexane at the platinum surface. They further implied that this altered pattern of adsorption is a geometric effect imposed by the zeolite. We propose that terminal adsorption, resulting in the formation of primary alkyl species, is favourable on the electron-rich Pt particles and that the observed importance of electron-richness or decreased electron deficiency of the platinum particles for the hexane aromatization reaction is due to this electronic effect on orientation in the adsorption. It has been found that the metal electron density determines the primary/secondary ratio of coordinated alkyls; electron-richness of metal gives rise to more anionic character of coordinated alkyls, preferring the primary type of alkyl species [28]. On the other hand, if alkyl species has radical or less anionic character as a result of less electron-rich character of the metal, secondary alkyl species should be more stable than primary alkyl species. This hypothesis may provide an explanation for the order of selectivity for benzene formation on the IE-KX series catalysts. On the IE-KF and IE-KCl catalysts, the presence of the electron-rich site of the Pt metal, as revealed by low C–O stretching frequency, should be advantageous to terminal adsorption of hexane, leading to high activity and selectivity for benzene formation. Non-terminal adsorption which may result in the MCP formation followed by the isomerization was effectively prevented. The Pt particles on the IE-KBr and IE-KI catalysts may not be electron-rich enough to enhance the probability of terminal adsorption of hexane. Thus on these catalysts selectivities for MCP and methylpentanes were considerably high, although they have no significant acidity so as to promote unwanted hydrocracking or isomerization reactions.

Thus it has been revealed that the halogen anions profoundly affect the electronic state of the Pt metal as well as its dispersion in KL zeolite. KF and KCl were effective in producing the site with high electron donating ability on the Pt particles in the KL zeolite, resulting in the excellent catalyst for hexane aromatization.

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