The effect of Fe on Pt particle states in Pt/KL catalysts

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A R T I C L E   I N F O
Article history:
Received 10 September 2014
Received in revised form 4 December 2014
Accepted 8 December 2014
Available online 15 December 2014

Keywords:
Fe-containing
Pt/KL
Pt states

A B S T R A C T
Two types of Fe-containing Pt/KL catalysts were prepared, characterized and examined using an n-hexane aromatization reaction. Pt/FeKL contained framework Fe, which was incorporated through hydrothermal synthesis, while Pt-Fe/KL contained non-framework Fe, which was introduced through impregnation. The differences between the framework and non-framework Fe were examined using XRD, FT-IR and Mössbauer spectroscopy. Pt dispersion and reducibility as well as the electronic states of the Fe and Pt particles were detected using H2-chemisorption, H2-TPR and XPS, respectively. With the non-framework Fe, an electron-rich platinum species (PtH+) formed after reduction. With the framework Fe, an electron-deficient platinum species (Pt0) was detected. The n-hexane aromatization results from adding 0.3 wt% non-framework Fe include conversion after 3.5 h on stream at 450 °C, H2/n-hexane = 3.0 (mole ratio) and 3 h−1 WHSV over the Pt-Fe/KL, which was maintained at 77%; these values are greater than the 41% Pt/KL and 25% Pt/FeKL. The Pt-Fe/KL benzene selectivity was 89%, which is also greater than the 83% Pt/KL and 55% Pt/FeKL. We discuss the effect of Fe on the Pt particle states and the relationship between the Pt states and catalyst activity.

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1. Introduction
Aromatics are mainly produced through catalytically reforming naphthas or light oil fraction pyrolysis and are important gasoline-blending stock and fundamental raw materials for producing plastics, plasticizers and synthetic resins, among other materials [1]. With rapidly increasing worldwide demand for aromatic, expanding the variety of raw materials for producing aromatics is acquiring significance. For example, the direct methane aromatization reaction can proceed through Mo/HZSM-5 and Mo/MCM-22 catalysts [2–4], and C2-C5 lower alkanes can be converted into aromatic compounds on high-silica pentasil-type zeolites that are modified with Ga and Zn, etc. [5–7]. Pt supported on alumina containing other metallic components, such as Re and Sn, is the commonly used catalyst for catalytic reforming. During this process, cycloalkane aromatization in naphtha is the main reaction; however, light C6+ alkanes conversion into aromatics is limited. Therefore, research on developing new processes and effective catalysts to convert light paraffins into aromatics is important.

Bernard et al. [8] reported on the Pt/KL catalyst, which has attracted widespread attention for its good catalytic performance in n-hexane aromatization. Azzam et al. [9] speculated that the hexane aromatization reaction is controlled by hexane diffusion into the wider KL zeolite channel lobs, where the Pt clusters reside. The controlled hexane diffusion inhibits bimolecular reactions that form coke and deactivate catalysts. Jacobs et al. [10] studied the effect of Pt cluster distribution on Pt/KL catalyst stability; they demonstrated that the Pt cluster size and location distribution was more important than dispersion on the activity and stability of the n-hexane aromatization reaction catalyst. Kumar et al. [11] found that high electron density on Pt stabilized by the basic zeolite support can discourage the metal–metal interaction and Pt agglomerate formation, which may reduce pore volume and catalytic activity.

The Pt particle characteristics are a key factor in Pt/KL catalyst performance [12,13]. Many studies have shown that electron-rich
Pt species aid in hexane aromatization through the Pt/KL catalyst [14–16]. The electronic state of the Pt on the Pt-supported catalyst is closely related to the carrier and surface species properties. Moroz et al. [17] found that a strong interaction between platinum and a highly efficient γ-Al2O3 support prevented full Pt reduction, which facilitated stabilization of the ionic Pt species and yielded a highly efficient n-heptane aromatization catalyst. Mironenkov et al. [18] proposed that, with an increase in the fraction of surface-bridging OH groups and an increase in the concentration of Lewis acid sites, platinum (IV) chloride complex anchoring on the support surface was accompanied by an increase in the fraction of outer-sphere complexes, which decreased Pt particle dispersion.

Promoters are commonly added to alter the electronic state of Pt and improve the Pt/KL catalytic activity. Cho et al. [19] reported that PtSn nanoparticles can form inside KL zeolite channels through Sn2+ ion exchange; therefore, the PtSn/KL catalytic performance during n-hexane aromatization can be improved mainly through a Pt ensemble effect by incorporating tin. Adding proper levels of rare earth elements (Gd, Tb, Dy, Tm or Yb) to a Pt/KL catalyst can increase Pt particle dispersion and aromatic selectivity [14,20,21]. Tatsunami et al. [22] greatly improved Pt/KL aromatization performance through adding KF and KCl, which effectively produced sites with a high-electron donating ability on the Pt particles. The halogen-treated Pt/KL catalyst studied by Fukanaga et al. [23] yielded more aromatics and greater aromatic selectivity than the Pt/KL catalyst; this catalyst also exhibited greater stability than Pt/KL due to the relatively slow carbon formation rate during the reaction.

Fe species (such as Fe2+) are common promoter components that can act as chemical anchors for noble metal particles during reduction and reaction and, thus, prevent active metal clusters from high mobility and larger aggregate formation [24]. Fe species can be introduced into catalysts using many methods; with an appropriate Fe ion valence and ionic radius, they can be incorporated into the zeolite framework during synthesis. Fe-containing microporous zeolites, particularly the MFI-type (Fe-ZSM-5 and Fe-silicalite), are highly efficient catalysts for many environmental relevant reactions, such as direct N2O decomposition and N2O reduction by CO [25]. On the other hand, Fe2O3 is always added into the catalysts through impregnation or co-precipitation method. PtFe/SiO2 samples prepared through incipient wetness impregnation using H2PtCl6 and Fe(NO3)3 precursors were more active than monometallic Pt/SiO2 for CO oxidation in air [26]. Zheng et al. [27] proposed that the bimetallic Pt-Fe/KL catalyst prepared through Fe co-impregnation into the Pt/KL catalyst performed better in both catalytic activity during n-hexane aromatization and sulfur resistance. Schmaue et al. [28] proposed that the interaction between the Fe2+ formed during reduction and Pt clusters was the likely origin for enhanced sulfur resistance and aromatization activity in the Pt/Fe/KL catalyst. Kobayashi et al. [29] reported that the Pt/Fe2O3-Al2O3 catalyst with Fe2O3 levels at approximately 7 wt% in the support exhibited much greater conversion and isolobtene selectivity for isobutane dehydrogenation than Pt/Al2O3. Their group proposed that adding Fe2O3 increased the surface Pt atoms’ electron density through Pt-Fe bimetallic particle formation.

In this paper, we studied two types of Fe-promoted Pt/KL catalysts. Framework and non-framework Fe-containing Pt/KL catalysts were prepared through hydrothermal synthesis and an impregnation method, respectively. We focused on the effect of these two different Fe species on Pt particle states and aromatization activity. The Fe and Pt species’ states were characterized using XRD, FT-IR, H2-TPR, H2-chemisorption, Mössbauer and XPS spectroscopy. The n-hexane aromatization reaction was performed in a continuous flow fixed-bed reactor.

2. Experimental

2.1. Sample preparation

2.1.1. Support preparation

KL zeolite was synthesized as follows: sodium aluminate (41 wt% Al2O3), KOH, and NaOH were dissolved in deionized water to generate solution A. Next, solution A was slowly added to a diluted colloidal silica solution (30 wt% silica sol and deionized water) with vigorous stirring until homogeneous gel B was obtained. Gel B was stirred for 10 h at room temperature and then transferred into a Teflon-lined autoclave. Crystallization was performed at 448 K under a static condition. After crystallization, the solid products were separated using suction filtration. After washing with distilled water, the products were dried in an air oven at 383 K and then calcined at 773 K for 5 h.

The framework Fe-containing KL zeolite with partial Al3+ replacement by Fe3+ in the framework position was prepared through hydrothermal crystallization and is referred to as FeKL. For FeKL zeolite synthesis, a ferric nitrate [Fe(NO3)3·9H2O] solution was added to gel B with stirring until dark brown gel C was formed. Gel C was incubated using the same procedures for the KL zeolite. The experimental details on the initial gel composition, temperature and crystallization period are listed in Table S1 in the Supplementary data.

The non-framework Fe-containing KL zeolite was prepared through impregnating the KL zeolite with an aqueous ammonium ferric nitrate (CeH10FeNO3) solution. The Fe loading was 0.3 wt%. This support is referred to as Fe/KL to distinguish the Fe species added through impregnation from the FeKL. After incubating at room temperature for 12 h, the Fe/KL sample was dried at 393 K for 12 h and calcined at 623 K for 5 h.

2.1.2. Catalyst preparation

The 0.5 wt% Pt was incorporated through incipient wetness impregnation using an aqueous Pt(NH3)2Cl2 solution at room temperature. After Pt impregnation, the samples were maintained at room temperature for 12 h and then dried at 393 K for 12 h. Next, calcination was performed in a muffle furnace at 623 K for 5 h. The Pt/KL without iron was also prepared for comparison. The catalyst compositions are listed in Table 1.

2.2. Characterization

An X-ray fluorescence (XRF) analysis was performed using a Philips Magix601 X-ray fluorescence (XRF) analysis apparatus. X-ray powder diffraction (XRD) patterns were recorded using a PANalytical X’Pert PRO diffractometer fitted with Cu Kα radiation (λ = 1.5418 Å), which operated at 40 mA and 40 kV. FT-IR spectra for samples in the structural vibration region were recorded using a Bruker TENSOR 27 FT-IR spectrometer. We recorded 57Fe Mössbauer spectra for the catalysts using a Topologic 500A spectrometer and proportional counter at room temperature. 57Co (Rh) moving in a constant acceleration mode was the radioactive source. Chemisorption of hydrogen was carried out using the Micromeritics AutoChemII2920. The catalysts were reduced at 673 K and cooled to 313 K in He. Ten percent H2/Ar was added in pulses at equal time intervals into an Ar flow until the peaks were equal. The average Pt particle sizes were calculated assuming a semispherical Pt particle and H2/Pt surface = 1. H2-TPR experiments were performed using the Micromeritics AutoChemII2920 in a 10% H2/Ar atmosphere (50 ml/min); the temperature was increased from 353 K to 923 K at a 10 K/min heating rate. The X-ray electron spectroscopy (XPS) measurements were performed using the VG ESCALAB MK2 photoelectron spectrometer system with Al Kα radiation (hν = 1486.6 eV). The residual pressure inside the
2.3. Catalytic reaction

The n-hexane aromatization reaction was performed in a fixed bed reactor at atmospheric pressure, 723 K. H2/n-hexane = 3.0 (mole ratio) and a 3 h⁻¹ weight hourly space velocity (WHSV). The catalyst pellets were crushed and sieved to yield particle sizes between 20 and 40 mesh. The catalysts were pre-reduced at 723 K under flowing hydrogen at 100 mL/min for 2 h. Next, n-hexane was added using a syringe pump. The products were analyzed online using a Varian 3800 GC equipped with an OV-101 column and flame ionization detector (FID).

3. Results and discussion

3.1. Fe states

The KL and FeKL zeolite chemical compositions are listed in Table 2. In aluminosilicate zeolites, cations are necessary to balance the framework negative charge on AlO₄⁻. Therefore, the K/Al ratio of KL zeolite is typically greater than 1. When a portion of the Al³⁺ in the KL zeolite framework is substituted by Fe³⁺, the K/(Fe + Al) ratio would also be greater than 1. With sufficient Fe³⁺ outside of the zeolite framework, the K/(Fe + Al) ratio would be less than 1. The K/(Fe + Al) ratio in the FeKL sample was 1.19, and the Fe/(Fe + Al) was 0.13; thus, approximately 13% (mole ratio) of the Al atoms were replaced by Fe atoms in the FeKL samples.

The KL, Fe/KL and FeKL sample XRD patterns are shown in Fig. 1. The sample patterns show characteristic diffraction peaks for the fully crystalline LTL zeolites (PDF no. 00-039-0224) in Fig. 1a. We did not detect peaks that were attributed to impurities and Fe₂O₃. The hkl(1 0 0) position, which is the most prominent peak for each crystalline zeolite, exhibited differences (Fig. 1b). The Fe/KL sample exhibited approximately the same peak position as the KL sample; however, the XRD reflections for FeKL sample were slightly shifted to higher d values compared with the other samples. For the Fe/KL sample, Fe³⁺ was not introduced into the zeolite framework after impregnation, which did not significantly change the KL zeolite crystalline structure. For the FeKL sample, the XRD reflections shifted to higher d values, which suggests an overall increase in the unit-cell parameters when Fe is incorporated into the framework of KL zeolite framework. The XRD reflections should shift due to the change in the zeolite unit cell when a heteroatom is incorporated into the zeolite framework. Duke et al. [30] demonstrated extended substitution levels up to a 0.825 mole fraction when Al₂O₃ was replaced by Fe₂O₃ during FeKL synthesis where FeO₄²⁻ ions were used as a Fe³⁺ source. The interplanar d-spacing continuously increased as the iron levels increased due to a larger Fe³⁺ ionic radius (49 pm) compared with Al³⁺ (39 pm). Due to the longer Fe-O bond (1.97 Å), the Fe-modified KL zeolite unit cell parameters and volume increased linearly with increasing iron levels. A similar lattice expansion was also reported for isomorphous substitution of Al³⁺ with Fe³⁺ in the mordenite lattice [31].

The FT-IR spectra for KL (curve a), Fe/KL (curve b) and FeKL (curve c) are shown in Fig. 2a. The FeKL spectrum (curve c) shows that the typical bands, which are characteristic of the asymmetric T-O bond stretching vibrations in the framework vibration region (between 400 and 1200 cm⁻¹) [30], shifted toward lower wavenumbers. This shift is due to the longer Fe-O bond distance (1.97 Å) compared with the Al-O bond (1.75 Å) [32] and indicates Fe³⁺ incorporation into the zeolite lattice, which is consistent with the XRD pattern results.

We did not observe characteristic Fe₂O₃ bands (471 cm⁻¹ and 573 cm⁻¹) in the Fe/KL spectrum (curve b) likely because the Fe₂O₃ loading levels were too low. A shoulder band was observed at approximately 960 cm⁻¹ (Fig. 2b) in the FeKL spectrum (curve c) that was absent in the KL and Fe/KL sample FT-IR spectra; this 960 cm⁻¹ band can be attributed to the framework Si-O-Fe vibration [33]. Duke et al. [30] reported similar results, wherein a shoulder band appeared at approximately 978 cm⁻¹, and the relative intensity of this shoulder increased with increasing iron levels.

Mössbauer spectroscopy of ⁵⁷Fe atoms is ideal for studying the Fe state in Fe-containing zeolites. In the framework sites, iron is in a tetrahedral oxygen coordination; however, in non-framework sites, the iron was likely an octahedral iron oxide; certain Mössbauer criteria may be used to distinguish these two types of Fe species. Isomer shift (IS) is often used to distinguish ferrous and ferric iron; an IS < 0.3 mm/s at room temperature indicates tetrahedral ferric iron, but octahedral ferric materials generate an IS > 0.3 mm/s [34]. Quadrupole splitting (QS) values at approximately zero indicate tetrahedrally coordinated Fe³⁺ species; however, the asymmetric octahedrally coordinated Fe³⁺ species produce non-zero QS values [35].

The Fe/KL and FeKL sample Mössbauer spectra and parameters at room temperature are shown in Fig. 3 and tabulated in Table 3. The Fe/KL and FeKL curves show similarly narrow and asymmetric Lorentzian line widths at approximately 0.58 mm/s. This value indicates that the iron ions are distributed at sites with

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**Table 1**

<table>
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<tr>
<th>Sample</th>
<th>Support</th>
<th>Fe content/Fe loading in the supports (wt%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Pt loading (wt%)</th>
<th>Pt dispersion (%)</th>
<th>Pt particle diameter (nm)&lt;sup&gt;b&lt;/sup&gt;</th>
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<td>0.50</td>
<td>51</td>
<td>2.20</td>
</tr>
</tbody>
</table>

<sup>a</sup> The content of framework Fe incorporated by hydrothermal synthesis was detected by XRF; the loading of non-framework Fe introduced by impregnation was 0.3 wt%.

<sup>b</sup> Average Pt particle sizes, assuming homogeneous semispherical Pt particles.

**Table 2**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Compositions (mole ratio)</th>
<th>K/Al or K/[Fe + Al]</th>
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<td>FeKL</td>
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<td>0.87</td>
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**Table 3**

<table>
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<tr>
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<th>Average IS (mm/s)</th>
<th>QS (mm/s)</th>
<th>Linewidth (mm/s)</th>
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<td>0</td>
<td>0.5820</td>
</tr>
<tr>
<td>Fe/KL</td>
<td>0.3398</td>
<td>0.7846</td>
<td>0.5837</td>
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</table>
homogenous chemical environments. For the Fe/KL sample, the IS was 0.3398 mm/s, and the QS was 0.7846 mm/s, which suggests octahedrally coordinated Fe$^{3+}$. The FeKL curve exhibits a singlet with a 0.2058 mm/s average IS, which indicates an Fe$^{2+}$ tetrahedrally coordinated by oxygen. These results indicate different Fe species states for the two Fe-containing zeolites.

3.2. Interaction between Fe and Pt

We used TPR experiments to study the reducibility of metals and the interaction between the Pt and supports. The TPR curves for the supports are shown in Fig. 4a, and the $\alpha$-Fe$_2$O$_3$ curve is shown in Fig. S1 in the Supplementary data for comparison. $\alpha$-Fe$_2$O$_3$ should be reduced to Fe$_3$O$_4$ and FeO + Fe at the temperature range 256–680 K and a 10 K/min heating rate [36]. Only two small hydrogen consumption peaks were observed at approximately 700 K and 870 K; these two peaks might be due to reduction of certain metal impurities in the zeolite. The Fe/KL curve exhibits a broad peak at the temperature range 523–703 K, which can be ascribed to Fe$^{3+}$ reduction out of the framework. This temperature was much lower than for the $\alpha$-Fe$_2$O$_3$ reduction because the chemical environment of the Fe$^{3+}$ species differed. A weak peak was observed in the FeKL curve at the higher temperature range 700–850 K. The FeKL zeolite XRD crystallinity was maintained after the TPR experiment (Fig. S2 in Supplementary data), which indicates that this TPR band can be ascribed to the reduction of trace levels of non-framework Fe$^{3+}$, which did not affect the FeKL stability. However, the temperature range of this peak was higher than Fe/KL, which suggests a non-framework Fe$^{3+}$ species having stronger interaction with the zeolite.

The catalyst’s TPR curves are shown in Fig. 4b. In the Pt/KL curve, a broad reduction peak appeared at approximately 503 K with a shoulder at 448 K and a weak peak at 657 K. For the Pt-Fe/KL sample, the peak at 503 K moved toward a higher temperature (513 K), and the shoulder band at 448 K disappeared. Two weak peaks appeared at 679 and 781 K. In the Pt/FeKL curve, only one Pt reduction peak was observed in a narrow temperature range with the maximum at approximately 473 K.

The peaks at different temperatures may be explained by metals in different states. Grau et al. [37] proposed that the broad peak
in the Pt/KL curve included reduction of both the PtO and PtO$_2$ species, and the shoulder peak must be related to a more easily reduced platinum species. Weak peaks at the temperature range 600–830 K may be attributed to trace levels of Pt species that are difficult to reduce. One broad reduction peak was observed in the Pt-Fe/KL curve, in contrast to two separate peaks (Pt at 503 K and Fe at approximately 623 K). The reduction temperature for this peak was slightly higher than for the Pt/KL, but significantly lower than for Fe/KL. These observations demonstrate that non-framework Fe$^{3+}$ can be reduced at a much lower temperature in the presence of Pt. Further, the observations herein confirm the interaction between the Pt and Fe oxide species [27,28], which yielded more uniform Pt particles states and a stronger Pt-support interaction. For the Pt/FeKL sample, the Pt reduced more easily at lower temperatures than for the Pt/KL and Fe/KL catalysts.

**Fig. 5.** XPS spectra of Fe2p and Pt4f of Fe-containing catalysts.
approximately 473 K, which indicates a weaker interaction between the Pt and FeKL zeolite. We suggest that the Fe not only affected the relative population of the different platinum species forms but also the platinum-support interaction. The strong metal-support interaction may discourage interactions among Pt particles and Pt agglomerate formation [11].

Platinum particle dispersion and the average platinum particle diameter after reduction at 673 K were determined using H₂ chemisorption (Table 1). The percent Pt dispersion and average Pt size in Pt-Fe/KL were 51% and 2.20 nm, which is greater than Pt/KL with 45% dispersion and a 2.51 nm average Pt particle size. However, upon incorporating the framework Fe, the Pt/FeKL dispersion decreased to 43%, and the average Pt particle size increased to 2.65 nm. Many studies have demonstrated that aromatization performance depends on the Pt particle size [38–40]. Platinum particles smaller than 2.5 nm are considered active sites for n-hexane aromatization [41]. Combining the H₂-TPR results, we demonstrate that adding the proper levels of non-framework Fe favors greater Pt dispersion and strengthened the Pt-support interaction.

The XPS analysis yielded more information on the chemical state of the metal particles at the catalyst surface. The binding energies that correspond to Fe2p₃/₂ and Pt4f₇/₂ were used to characterize the surface states of iron and platinum before and after reduction (Fig. 5). The catalysts that calcined at 623 K were designated Pt/FeKL(o) and Pt/Fe(KL(o)), and the catalysts that reduced at 723 K were designated Pt/FeKL(r) and Pt-Fe/KL(r). The Fe2p₃/₂ binding energy (710.1–711.7 eV) corresponded to Fe²⁺ [42,43] in the Pt/FeKL(o), Pt/FeKL(r) and Pt-Fe/KL(o) samples. Further, the value 709.5 eV was assigned to Fe²⁺ in the Pt-Fe(KL(r)) sample. These results suggest that Fe²⁺ was stabilized in the FeKL zeolite framework; however, the non-framework Fe³⁺ reduced to Fe²⁺ after reduction.

The Pt4f₇/₂ binding energies of the Pt/FeKL(o) and Pt-Fe/KL(o) (72.2 eV) were similar to the corresponding Pt⁰ (72.5 eV) [15], which indicates that the Pt particles on these two types of Fe-containing catalysts were in the same chemical state before reduction. After reduction, the Pt/FeKL(r) binding energy (71.6 eV) was higher than the binding energy that corresponds to Pt⁰ (71.0 eV) [43] and Pt/KL (71.1 eV) [44], which indicates the presence of electron-deficient platinum species (Pt⁰⁺) on this catalyst. This electron-deficient Pt⁰⁺ might be due to the structural defects in FeKL, which were generated during synthesis. However, the value for the Pt-Fe/KL(r) (70.9 eV) was lower than for Pt⁰ (71.0 eV), which indicates the presence of electron-rich Pt species (Pt⁰⁻) outside the zeolite due to the interaction between the platinum particles and electron-donor sites at the surface.

The electronic states of the Pt clusters after reduction differed greatly. The Pt particles in the Pt/KL sample were similar to Pt⁰ [15]. The highest population of electron-rich platinum species (Pt⁰⁻) was observed in Pt/FeKL, but the highest concentration of electron-deficient platinum species (Pt⁰⁺) was observed in the Pt/FeKL sample. The order of electron density on the Pt clusters was Pt-Fe/KL > Pt/KL > Pt/FeKL, which is consistent with the order of Pt dispersion. We believed that the higher electron density of the Pt clusters in the Pt-Fe/KL catalyst is due to the electron-donor sites generated by the Fe²⁺ that forms after reduction.

### 3.3 Catalytic activity

Fig. 6 shows the catalysts’ activity and benzene selectivity during n-hexane aromatization at 723 K after 1 h on stream. The Pt/KL catalyst exhibited good benzene selectivity at 82% and moderate conversion at 50%. With 0.3 wt% Fe added, the Pt-Fe/KL catalyst conversion and aromatization selectivity were much greater (76% conversion and 86% benzene selectivity) than for other catalysts. When Fe was incorporated into the zeolite framework, the Pt/FeKL catalytic performance significantly decreased. The hexane conversion of this catalyst was approximately 30% and the benzene selectivity was only 52%.

The product distribution at 723 K for 3 h on stream using the three catalysts is summarized in Table 4. The major reaction products formed from n-hexane with H₂ at 723 K were benzene, hexane isomers (iso-C₆), C₁–C₅ hydrocarbons (hydrogenolysis and hydrocracking products) and alkenes. The Pt/Fe/KL catalyst exhibited the best n-hexane aromatization performance. The benzene yield was 65% for 3 h on steam. The benzene yield was low for the Pt/FeKL catalyst, but more dehydrogenation (alkene) and isomerization (iso-C₆) products were produced; these results may be related to the FeKL acid sites, at which dehydrogenation and isomerization can proceed through the carbenium ion mechanism. Moreover, the greater number of isomerization products might also be due to the increase in FeKL zeolite unit-cell parameters, which yielded enhanced 1–5 ring closure [45].

The order of aromatic activity and benzene selectivity, Pt-Fe/KL > Pt/KL > Pt/FeKL, paralleled the Pt particle electron density on the catalysts. These results support the conclusion that higher Pt particle electron density yields higher dehydrocyclization activity in Pt/KL catalysts [15]. The Pt electronic structure is 5d⁶6s¹ and includes two unpaired electrons. When the electrons were transferred to Pt particles, the Pt catalysts’ aromatic properties increased with a decrease in unpaired electrons [14]. Grau et al. [16] reported a similar result for n-heptane aromatization using barium-doped Pt/KL catalysts. Electron enrichment in the Pt clusters was observed with well dispersed and distributed BaO throughout the zeolite. We suggested that more electron-rich Pt particles were formed after reduction due to partial electron transfer from Fe²⁺ ions to Pt⁰. The high Pt electron density may encourage metal-metal interactions and Pt agglomerate formation. Consequently, this Pt-Fe/KL catalyst
exhibited better performance in both catalytic activity and benzene selectivity during n-hexane aromatization.

4. Conclusion

Our results show that introducing Fe into the KL zeolite influenced the zeolite KL structure and chemical state. When Pt was loaded onto the Fe-containing zeolites, the platinum dispersion and electronic states that affected the Pt/KL catalyst aromatization performance differed significantly after reduction. Electron-rich platinum species (Pt\textsuperscript{0}) were detected with non-framework Fe, which favored higher Pt dispersion and smaller Pt particle size. Conversely, partial substitution of Al by Fe in the KL zeolite framework favored formation of electron-deficient platinum species (Pt\textsuperscript{II+}) with lower dispersion and bigger particle size. These differences in Pt dispersion and electronic states affected the containing-Pt/Fe/KL catalysts’ aromatization performances. As shown by the n-hexane aromatization test, the order of aromatic activity and benzene selectivity for n-hexane aromatization, Pt-Fe/KL > Pt/KL > Pt/FeKL, was consistent with the catalysts’ Pt particle electron density. These results indicate that adding a Fe promoter is effective for adjusting the electronic states of Pt particles, which are closely related to the Pt/KL catalyst activity and selectivity.

Acknowledgements

We thank Prof. Junhu Wang, Ms. Yanjie Wang and Prof. Shishan Sheng for help in \textsuperscript{57}Fe Mössbauer spectroscopy and XPS analysis.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2014.12.017.

References


Table 4

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<td>0.69</td>
<td>12.30</td>
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</table>

T = 723 K; WHSV = 3 h\textsuperscript{-1} and H\textsubscript{2}/n-C\textsubscript{6} = 3.