

Effect of Hydrohalogenation of PtRe/H-ZSM-5 for Cyclohexene Conversion

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Abstract: Extended use of supported Pt catalysts causes thermal migration of Pt particles to form large agglomerates, thus decreasing the catalytic activity. The combination of Pt with Re protects Pt against migration. In addition, Cl⁻ injection into the reactor assists Pt particles redispersion to prolong catalyst life. In this work, a PtRe/H-ZSM-5 catalyst was treated with either HCl or HF to investigate their role in activating or deactivating the catalyst. The conversion exceeded 90% in the whole temperature range with the PtRe/H-ZSM-5(HCl) catalyst, and its activity for the direct isomerization of cyclohexene to methylcyclopentenes (MCPEs) was the lowest but the activity for the hydrogenation of the MCPEs to methylcyclopentane was the highest. The reactivities of MCPEs and cyclohexadienes on the catalysts were similar because both are dehydrogenation reactions. Benzene production was significantly higher on the hydrochlorinated catalyst than on the other catalysts, and its hydrocracking activity was the lowest, which is a good characteristic for processing catalysts where cracking is undesired.

Key words: platinum; rhenium; cyclohexene; hydroconversion; hydrofluorination; hydrochlorination; H-ZSM-5 zeolite

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Cyclohexene (CHE) conversion on bifunctional catalysts goes through a number of reactions that each requires a different active site type. Hence, CHE is frequently selected as a probe molecule for characterizing catalyst preparation [1–4]. The experimental conditions, temperature and presence or absence of hydrogen and the pressure of hydrogen, have important effects on the catalytic behavior. In the absence of hydrogen, disproportionation [5,6] and dehydrogenation [7,8] reactions take place. The former reaction gives benzene and cyclohexane (CHA) and the reaction is hydrogen transfer. When the reaction is carried out in the presence of metal catalysts, CHE behaves as both hydrogen donor and acceptor. If the metal is supported on Al₂O₃ [9], the acid sites are weakly Lewis acid and not strong enough to promote carbonium ion formation, and hence isomerization and cracking reactions do not occur (monofunctional catalyst). The use of the H-form of zeolites, which possess strongly acidic Brønsted and Lewis sites, can promote CHE isomerization to a mixture of methylcyclopentenes (MCPEs) and cracking to lower molecular mass hydrocarbons and the reaction scheme is more complicated (bifunctional catalyst). However, the treatment of the cation-exchanged zeolites with aqueous HCl or HF acid leads to loss of cations and partial dealumination of the zeolite framework.

Isomerization of CHE over very pure alumina with and without Cl⁻ ions has been studied by Ozimek et al. [10,11].

Introducing Cl⁻ ions into aluminate aluminas in different ways causes Brønsted acid sites to appear, and both skeletal isomerization and total conversions were much increased [12].

CHE hydrogenation and dehydrogenation are much faster than benzene hydrogenation and CHA dehydrogenation on noble metal catalysts. Aboul-Gheit and coworkers have studied aromatic hydrogenation [13], hydroconversion of *n*-paraffins in light naphtha [14], cyclohexane dehydrogenation [15] and hydroisomerization, hydrocracking and dehydrocyclization of *n*-paraffins [14,16] using Pt/Al₂O₃ catalysts promoted with other metals (Rh, Ir, Re or U) and Cl⁻ or F⁻. Rhenium is a promoter for platinum in catalysts for petroleum naphtha hydroisomerization and reforming used for upgrading octane numbers. Although Pt-Re catalysts have received enormous attention since the discovery of the Re promotion effect by Klusdahl [17], monometallic Re catalysts have not received much consideration. Researches on Pt promoted by Re were mainly concerned with catalyst protection to extend its lifetime. However, these catalysts are also conventionally treated with injected light chlorohydrocarbons to generate HCl, which improves catalyst acidity and Pt dispersion. Since Klusdahl [17] showed that Re addition to platinum is required to give superior petroleum naphtha reforming catalysts, the most commercially successful bimetallic catalysts used in refineries contain Pt-Re

combinations [18–20].

CHE hydrogenation and dehydrogenation have been investigated using Ni, Pt, Rh, and Pd catalysts [6, 8, 21–28]. CHE hydroconversion over catalysts containing 0.35 wt% of the single metals Rh, Pt, Ir, Re, and their combinations on γ -Al₂O₃ was carried out at temperatures of 50–250 °C [9]. The effect of doping with 3.0 wt% of Cl⁻ or F⁻ was examined. The bimetallic combinations gave more active catalysts than the monometallic catalysts. In the present work, a Pt-Re loaded H-ZSM-5 catalyst was treated with 3.0% HCl or HF to examine their effects on CHE hydroconversion in a flow reactor operated in presence of hydrogen at 50–400 °C.

1 Experimental

1.1 Catalyst preparation

1.1.1 H-ZSM-5 catalyst

This catalyst was prepared by exchanging Na-ZSM-5 zeolite with 0.6 mol/g NH₄NO₃ solution followed by drying at 110 °C overnight and calcination at 550 °C for 4 h. The Na-zeolite was provided by Süd Chemie, München, Germany. The catalyst had a Si/Al molar ratio of 23.8, specific surface area of 440 m²/g, and pore volume of 0.16 cm³/g. The H-form had a sodium content < 0.002%.

1.1.2 PtRe/H-ZSM-5 catalyst

The PtRe/H-ZSM-5 catalyst was prepared by two successive impregnations: first with an aqueous solution of hexachloroplatinic acid followed by a second impregnation with ammonium perrhenate to give 0.35 wt% Pt + 0.35 wt% Re in the finished catalyst. The catalyst was dried and calcined as in Section 1.1.1 after each impregnation. It was reduced in a hydrogen flow in the catalytic reactor at 500 °C for 8 h before the reaction.

1.1.3 PtRe/H-ZSM-5(HCl) catalyst

The PtRe/H-ZSM-5 catalyst prepared in section 1.1.2 was doped with a solution containing the required quantity of HCl acid to give 3.0% HCl. The catalyst was then dried, calcined, and reduced as above.

1.1.4 PtRe/H-ZSM-5(HF) catalyst

The PtRe/H-ZSM-5 catalyst prepared in section 1.1.2 was doped with HF solution sufficient to give 3.0% HF. It was dried, calcined, and then reduced as above.

All the catalysts basically retained the crystallinity of the original H-ZSM-5 zeolite, which was shown by X-ray dif-

fraction (XRD) analysis. The main diffraction peak in all forms appeared at 2θ of 23.0°. However, a very slight increase in the diffraction peak at 2θ of 10.884° for the PtRe/H-ZSM-5(HCl) and PtRe/H-ZSM-5(HF) catalysts indicated a slight bulk dealumination of the H-ZSM-5 zeolite.

1.2 Hydroconversion reactor and product analysis

The reactor was a silica glass tube containing 0.2 g catalyst heated in an insulated wider silica tube jacket thermostated to ± 1 °C. Hydrogen gas was used as a carrier and simultaneously as a reactant at a flow rate of 20 ml/min in all runs. The feed (CHE) was introduced into the reactor using a H₂ flow passed into a closed jar thermostated at a fixed temperature of 28 °C whereby the quantity of cyclohexene fed to the catalyst was 8.33×10^{-3} mol/h, i.e., the H₂/CHE molar ratio was 6.4 in all runs. The amount of CHE condensed between saturator and reactor was considered in calculating the actual mass of CHE flowing over the catalyst. The reaction temperatures were 50–400 °C, at 25 °C decrements starting from 400 °C downwards. The gaseous reaction effluent from the reactor was injected into a Perkin-Elmer Autosystem XL gas chromatograph with a 15 m capillary column of Carbowax 20M bonded in fused silica and analyzed using a FID detector and a Turbochrom Navigator program. The GC column separated the product effluent into hydrocracked components, MCPes, methylcyclopentane (MCPA), CHE, CHA, cyclohexadienes (CHDEs) (1,3- and 1,4-), and aromatics (benzene, toluene, and xylenes). The examination after a time on-stream of 180 min at 400 °C did not show any decrease in the activity of the catalyst. Moreover, examination of the catalysts for carbon deposition using temperature-programmed oxidation (TPO) in a differential scanning calorimeter (DSC) did not show any CO₂ peak.

1.3 Catalyst characterization

The temperature-programmed desorption (TPD) of pre-sorbed ammonia on the acid sites of the zeolite supports was carried out in a DSC using nitrogen as a purge gas according to the procedure previously reported [29,30]. The NH₃ desorption enthalpy values from the higher temperature endothermic peak was used to correlate the acid site density of the three PtRe/H-ZSM-5 catalysts. The peak temperature was used to correlate the strength of these acid sites.

The dispersion of PtRe in the catalysts (metal fraction exposed) was determined by hydrogen chemisorption using a pulse technique similar to that used by Freel [31]. A known mass of a calcined catalyst was heated in the chemisorption furnace at 500 °C for 3 h in a flow of 50 ml/min of

ultra-pure hydrogen. The flow was then replaced by oxygen-free nitrogen gas at 30 ml/min for 2 h at 500 °C (degassing). The furnace was shut off and the catalyst was cooled to room temperature. Hydrogen was then pulsed into the nitrogen carrier till saturation, i.e., until the appearance of hydrogen peaks corresponding to complete non-adsorbed pulses. The hydrogen uptake was calculated as hydrogen atoms adsorbed per total Pt-Re atoms on the basis of 1:1 stoichiometry.

The X-ray diffraction (XRD) patterns of the catalysts were carried out using a Phillips X, Pert Diffractometer PW 1390 at 40 kV and 30 mA with Ni Filter and Cu K_{α} radiation. The XRD measurements were carried out up to 2θ of 60°. The XRD patterns obtained (not given here) for the catalysts showed fairly similar intensities for the diffraction peaks. The main crystalline peak appeared in all samples at 2θ of 23.0°. The HCl and HF doped samples showed slightly higher relative intensity of the lowest 2θ peak, indicating slight dealumination of the zeolite support.

2 Results and discussion

Light organic chlorohydrocarbons are normally injected into the industrial reactors used in the light naphtha hydroisomerization process. This procedure is applied for the catalyst chlorination with commercial Pt/Al₂O₃ catalysts since these chlorohydrocarbons produce HCl and small hydrocarbons at higher temperatures. The HCl formed assists the redistribution of the platinum crystallites and inhibits their growth into agglomerates, besides enhancing the acidity of the catalyst. This treatment differs from that normally applied in preparing chlorinated Pt/zeolite catalysts where the support is first halogenated before impregnating or exchanging with a Pt precursor. The use of the hydrofluorination of noble metal-containing catalysts may be an alternative for HCl doping because the Al-F bond is stronger than the Al-Cl bond and the requirement for the continuous injection of a fluorohydrocarbon into the reactor is therefore unnecessary.

The metal mainly used in light naphtha hydroisomerization and heavy naphtha reforming catalysts is platinum. However, another metal such as Ir, Re, Pd, Ti or Sn is normally combined with Pt in the catalyst, mainly to improve the catalyst lifetime by restricting Pt agglomeration, sulphur poisoning and deactivation by carbon deposition. It is important to know the behavior of the promoter metal towards the presence or absence of HCl or HF when the metal is supported on H-ZSM-5 zeolite. In the present work, the doping of PtRe/H-ZSM-5 catalysts with HCl or HF was investigated with the hydroconversion of CHE.

2.1 Effect of hydrochlorination or hydrofluorination

on the PtRe/H-ZSM-5 catalyst

With 3.0% HCl doping, the acid site density (Table 1) was enhanced ($\Delta H_d = 96.0$ J/g) over that of the untreated catalyst ($\Delta H_d = 90.9$ J/g). Hydrofluorination gave a lower density of acid sites ($\Delta H_d = 94.2$ J/g) than hydrochlorination. However, the effect of hydrofluorination was higher than hydrochlorination for enhancing the strength of the acid sites, with the ammonia desorption peak temperature being in the order of PtRe/H-ZSM-5(HF) > PtRe/H-ZSM-5(HCl) > PtRe/H-ZSM-5.

Table 1 NH₃-TPD, and Re and Pt-Re dispersion by H₂ chemisorption in the Re/H-ZSM-5 and PtRe/H-ZSM-5 catalyst

Catalyst	Acid site strength distribution		
	ΔH^a /(J/g)	Peak temperature ^b (°C)	Metal dispersion (%)
Re/H-ZSM-5 ^c	90.9	380.1	56.8
Re/H-ZSM-5(HCl) ^c	99.6	392.3	59.8
Re/H-ZSM-5(HF) ^c	105.3	415.7	63.8
PtRe/H-ZSM-5	90.9	376.1	58.8
PtRe/H-ZSM-5(HCl)	96.0	390.3	63.5
PtRe/H-ZSM-5(HF)	94.2	395.9	60.8

^aProportional to acid site number.

^bProportional to acid site strength.

^cReference 32.

Treating PtRe/H-ZSM-5 with the acids affected Pt-Re dispersion (Table 1). With the HCl treatment, the metal dispersion was increased over that using the HF treatment. The dispersion order was PtRe/H-ZSM-5(HCl) > PtRe/H-ZSM-5(HF) > PtRe/H-ZSM-5.

The comparison of the properties of the Re/H-ZSM-5 [32] and PtRe/H-ZSM-5 catalysts (Table 1) before and after HCl or HF treatments indicated that dispersion of either mono-metal (Re) or bimetal (Pt-Re) in the H-ZSM-5 support was increased after halogenation. Also, the acid site number (ΔH_d) and strength (NH₃ peak temperature) were increased by this treatment. Hydrofluorination was significantly more effective than hydrochlorination when the catalyst contained Re alone. In case of the PtRe/H-ZSM-5 catalyst, the HF-treated case was less significantly affected than the HCl-treated version for both metals dispersion and acidic properties. Since HF is a stronger acid than HCl, it can be assumed that the combination of Pt and Re is not as good for metal dispersion and acidity than when Re was loaded alone in the zeolite. Pt when present with Re seems to have played a role in diminishing the spreading of the metal on the surface of the zeolite as well as blocking of the acid sites. This can be attributed to that the deposition of fluoro-silicon and fluoro-aluminum debris was more than that of chloro-aluminum debris.

In our recent work [33], pore volume distribution curves

for catalysts containing 2% Pt/H-ZSM-5 before and after doping with 4% HF for the alkylation of toluene with methanol were shown. In the catalyst treated with 4% HF, the large pores in the volume distribution curve (in the range of 2.7–5.5 nm) had lower values than those of the untreated catalyst, while the smaller pores (0.3–2.7 nm) has higher values. This was attributed to the filling of most of the large pores by the debris formed from the leaching of Al and Si at 4% HF concentration.

2.2 Effect of HCl or HF doping of PtRe/H-ZSM-5 catalyst on the conversion of cyclohexene

The distribution of the CHE hydroconversion products using the PtRe/H-ZSM-5, PtRe/H-ZSM-5(HCl) and PtRe/H-ZSM-5(HF) catalysts are shown in Fig. 1. The general features are a continuous decrease of CHE with reaction temperature and an increase of CHA at 50–200 °C. At intermediate temperatures, MCPEs, and MCPA passed through maxima at 300–325 °C, beyond which they de-

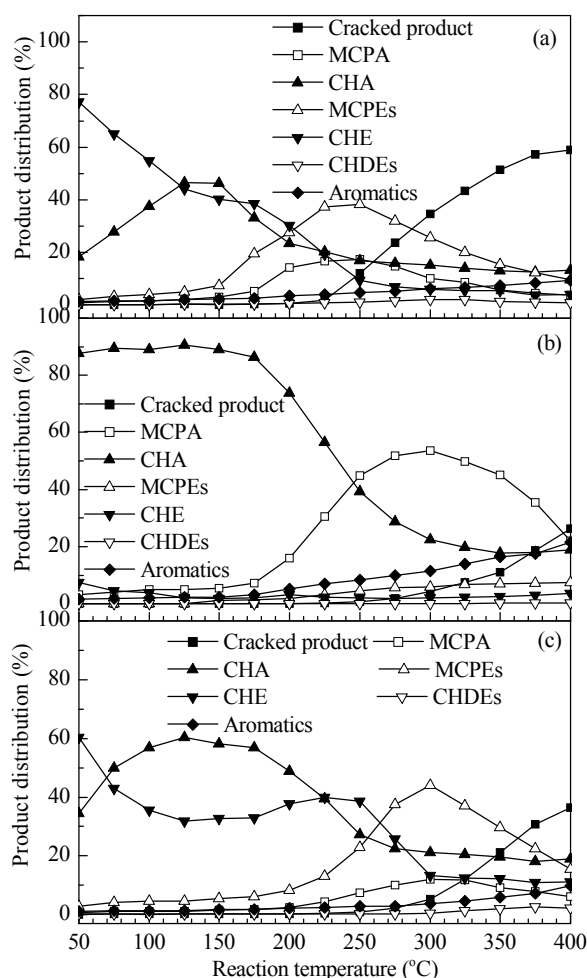


Fig. 1. Distribution of cyclohexene hydroconversion product with PtRe/H-ZSM-5 (a), PtRe/H-ZSM-5(HCl) (b), and PtRe/H-ZSM-5(HF) (c).

creased. At higher temperatures, CHE dehydrogenation to aromatics via CHDE formation and hydrocracking to lower molecular mass hydrocarbons increased continuously with temperature.

Figure 1(b) exhibited a distinct variation where the MCPEs comprises ~90% of the product between 50 and 175 °C, beyond which these cycloolefins decline to < 20% at 400 °C. Another major product was MCPA, the hydrogenation product of MCPEs, which reached a maximum of ~50% at 300 °C beyond which it declined to ~20% at 400 °C. All other intermediates were generally less.

Figure 2 compares the CHE hydroconversion activities of the PtRe-containing catalysts as a function of reaction temperature. The highest activity was given by the HCl treated catalyst in the whole reaction temperature range of 50–400 °C. The lowest activity was given by the untreated catalyst at low reaction temperatures. However, at 200–400 °C, the HF treated catalyst became the least active.

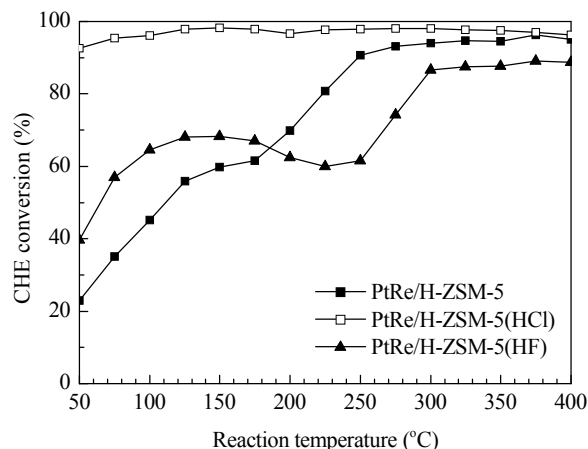


Fig. 2. Hydroconversion of cyclohexene using different catalysts.

2.3 Hydrogenation of CHE to CHA

CHE is an unsaturated hydrocarbon molecule, and its initial adsorption is largely through the most energetically favorable donor π and acceptor π^* orbitals with the appropriate metal surface orbitals. On an atomically flat surface, CHE can form a chemisorption state in which the C_6 -ring is oriented in a plane parallel to the surface plane. The first reaction of chemisorbed CHE, taking place at low reaction temperatures, is its exothermic hydrogenation to CHA. Thus, the hydroconversion activity of CHE (Fig. 2) can be attributed mainly to its hydrogenation to CHA (Fig. 3) throughout the low temperature range (50–200 °C). The activities of the catalysts are in the order of PtRe/H-ZSM-5(HCl) > PtRe/H-ZSM-5(HF) > PtRe/H-ZSM-5.

The hydrohalogenation treatment of the PtRe/H-ZSM-5 catalyst has greatly enhanced the reactivity for CHE hydro-

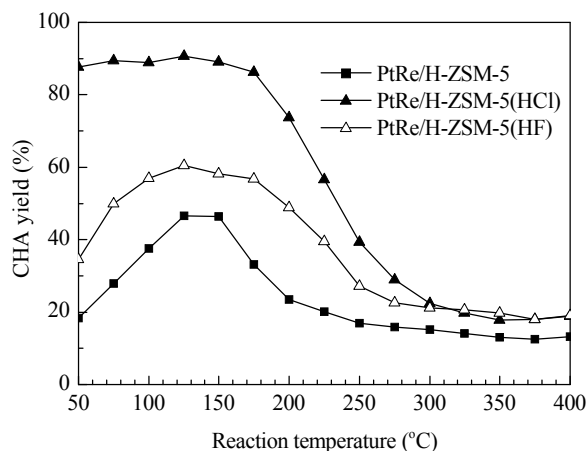


Fig. 3. Cyclohexane production using different catalysts.

genation. The HCl treatment had more effect than the HF treatment. Figure 3 shows that PtRe/H-ZSM-5 gave a maximum CHA production of 46.3% at 150 °C, while PtRe/H-ZSM-5(HF) gave a maximum of 60.0% at 125 °C, and PtRe/H-ZSM-5(HCl) exhibited the highest activity with ~90% in the temperature range 50–175 °C. Beyond 175 °C, with a further increase of temperature, the hydrogenation activity declined since the reaction equilibrium was reversed from exothermic hydrogenation towards endothermic dehydrogenation. The enhancement of the hydrogenation activity with the HF treatment can be attributed to: (1) A better dispersion of PtRe bimetal in the support from 58.8% to 60.8% (Table 1); (2) A decrease in the basic Lewis sites present originally in the H-ZSM-5 zeolite via neutralization with HF; (3) A stronger “inductive effect” on the neighboring hydroxyl groups due to the influence of fluoride ions adsorbed on the surface of the H-ZSM-5 support [12].

On the other hand, HCl-treatment of PtRe/H-ZSM-5 changed the behavior of CHE hydrogenation (Fig. 3) such that CHA in the product significantly exceeded those obtained with the other two catalysts, particularly in the lower temperature region. This implied a significant activity enhancement of the PtRe bimetal on the surface of the PtRe/H-ZSM-5(HCl) catalyst. Previous studies by Aboul-Gheit [34,35] showed that benzene hydrogenation was completely inactive on a 0.6% Re/Al₂O₃ catalyst under high hydrogen pressure and temperatures of 100–140 °C. This is evidence that Re by itself at a concentration of ~0.6% cannot act as a hydrogenation component.

Recently, Aboul-Gheit et al. [36] doped unloaded H-ZSM-5 zeolite with HCl or HF and found that the acid site number, strength and hydrogenation activity on the H-ZSM-5(HCl) and H-ZSM-5(HF) catalysts were increased, and H-ZSM-5(HCl) exhibited a significantly higher hydrogenation activity than H-ZSM-5(HF). This was attributed to a larger increase in the acid site number in the for-

mer catalyst although the acid site strength was more enhanced in the HF-treated catalyst. In the present study, the loading of H-ZSM-5 zeolite with PtRe resulted in the same response towards HCl and HF treatments. Arena et al. [12] showed that the Cl⁻ ion adsorbed on the surface of Al₂O₃ changes the electronic properties of the outer layer and decreases the basic Lewis sites. It also induces a stronger “inductive effect” on the neighboring hydroxyl groups on the zeolite surface, weakening the O–H bond, and rendering the proton more acidic. Le Van Mao et al. [37] has doped H-ZSM-5 zeolite with a low concentration of F⁻ species and found that its acidity was enhanced by forming new Brønsted acid sites, in addition to the strengthening of some acid sites of the parent zeolite.

Several authors have shown that acid sites in zeolites act as hydrogenation sites, particularly at higher temperatures. Sano et al. [38] reported that H-ZSM-5 zeolite becomes an active hydrogenating catalyst and it converts 95% of ethylene to ethane at a temperature of 535 °C. Because no metal impurity in the zeolite was detected, Sano et al. concluded that the hydrogenation took place on the acidic sites of the zeolite. Jacobs and co-workers [39] also concluded that the Brønsted acid sites of zeolites act as active hydrogenation sites at higher temperatures. Senger et al. [40] have provided a deeper insight into this type of catalytic hydrogenation that proceeds without the participation of a transition metal.

The higher activity of the HCl-treated zeolite compared with the HF-treated one can be attributed to a physical effect rather than a chemical effect. The higher strength of HF than HCl allows it to attack Si in the zeolite, causing it to form debris of fluoro-silicon species that deposit in the channels of the zeolite that causes diffusion restriction that decreases the ability of CHA to diffuse and react.

2.4 Isomerization of CHE to MCPEs and MCPA

Figure 4 depicts the yield of methylcyclopentenes (MCPEs) as a function of reaction temperature. With the fluorinated and untreated catalysts, these olefinic isomers increased with temperature to reach a maximum, beyond which they decrease with a further increase of temperature. However, with the HCl treated catalyst, MCPEs increased slowly with temperature up to 400 °C. The rates of formation of these isomers were in the order of PtRe/H-ZSM-5 > PtRe/H-ZSM-5(HF) > PtRe/H-ZSM-5(HCl). This order is the reverse of the order of the hydrogenation activities (Fig. 3). In other words, the yield of these MCPEs was higher with a less active hydrogenating catalyst and vice versa. Because these MCPEs are unsaturated isomers of CHE, they can be saturated to MCPA under the same reaction conditions. Hence, the more active hydrogenating catalysts will

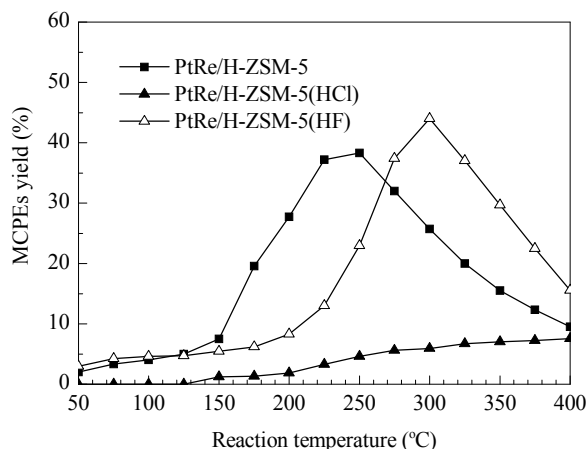


Fig. 4. MCPEs yield as a function of reaction temperature using different catalysts.

produce lower yields of MCPEs (Fig. 4). MCPEs products from the untreated and fluorinated catalysts were relatively high and reached their maxima (38.3% and 44.0%, respectively) at 250 and 300 °C, respectively.

In the hydrogenation of MCPEs to MCPA (Fig. 5), the three unsaturated isomers (MCPEs) of CHE are saturated giving CHA isomer. The overall isomerization activities of the catalysts equal the sum of unsaturated and saturated C5-ring containing compounds, i.e., MCPEs + MCPA (Fig. 6). Dwyer et al. [41] defined the relative rates of isomerization (monomolecular reaction) and bimolecular hydrogen transfer as follows:

$$\text{Isomerization/Hydrogen transfer} = I(\text{MCPEs} + \text{MCPA}) / I(\text{CHA} + \text{MCPA})$$

where I refers to the initial selectivity. Tjandra and Zaera [42] and Jolly et al. [43] have agreed with Dwyer et al., which indicates that the maximum of the isomerization from the six-membered ring to the five-membered one is not a critical catalyst specification. The reaction sequence in Eq.

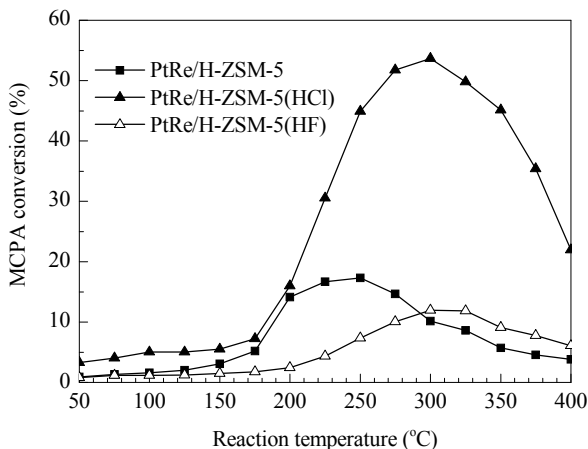


Fig. 5. MCPA conversion as a function of reaction temperature using different catalysts.

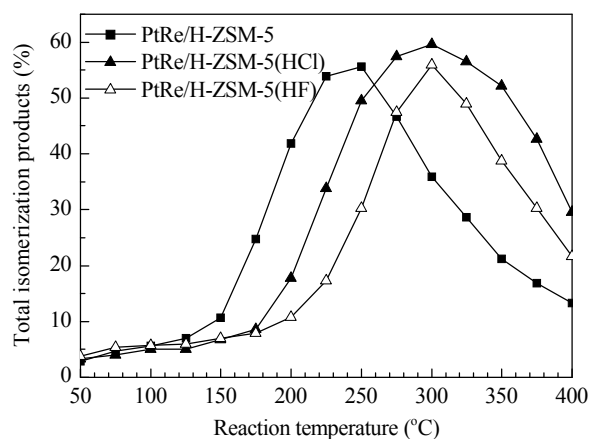


Fig. 6. Total isomerization products using different catalysts.

(1) shows that a molecule of CHE rearranges itself on an acid site to produce an equilibrium mixture of MCPEs, which are then hydrogenated on a PtRe site to produce a MCPA molecule.

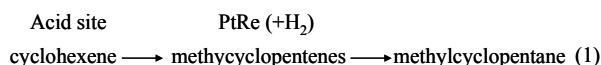


Figure 5 shows that the hydrogenation activity of the PtRe/H-ZSM-5(HCl) catalyst greatly exceeds that of the HF-treated and untreated catalysts. The maximum conversion of MCPA was 53.6% at 300 °C on the PtRe/H-ZSM-5(HCl) catalyst as compared with 11.9% and 17.3% on PtRe/H-ZSM-5(HF) and PtRe/H-ZSM-5 at 300 and 250 °C, respectively. These results are in agreement with the results of the hydrogenation of CHE to CHA (Fig. 3), and both orders were the same as the order of acid site number and strength as well as the PtRe dispersion (Table 1). The effect of Cl^- and F^- ions in the catalysts in decreasing the basic Lewis sites, a stronger inductive effect on the neighboring O–H bond, and rendering the proton more acidic should also contribute to these results.

2.5 Dehydrogenation of CHE to CHDEs

CHE first slowly dehydrogenates to a mixture of 1,3- and 1,4-CHDEs, then further dehydrogenates at higher rates with increasing temperature from 275 to 400 °C, since dehydrogenation is endothermic (Fig. 7, Scheme 1). Land et al. [44] assumed that CHE at low temperatures is bonded to a noble metal substrate as di- σ bonded CHE. This may undergo conversion analogous to olefin metathesis to form the bis-(alkylidene) and 1,6-hexadialkylidene. Furthermore, CHDEs dehydrogenate to benzene, which is the most stable dehydrogenation product.

Figure 7 shows the sum of 1,3- and 1,4-CHDEs in the product as a function of reaction temperature. With the untreated PtRe/H-ZSM-5 and PtRe/H-ZSM-5(HF) catalysts,

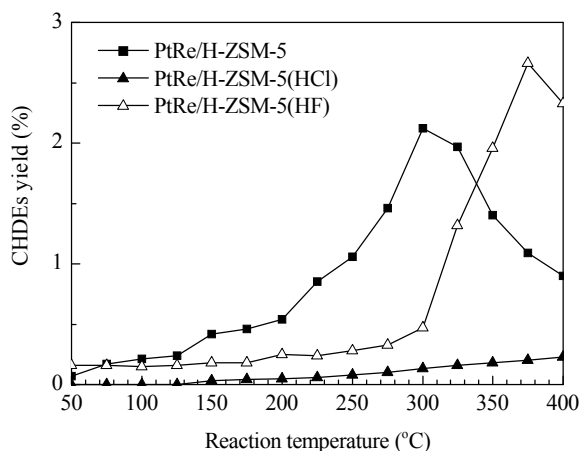
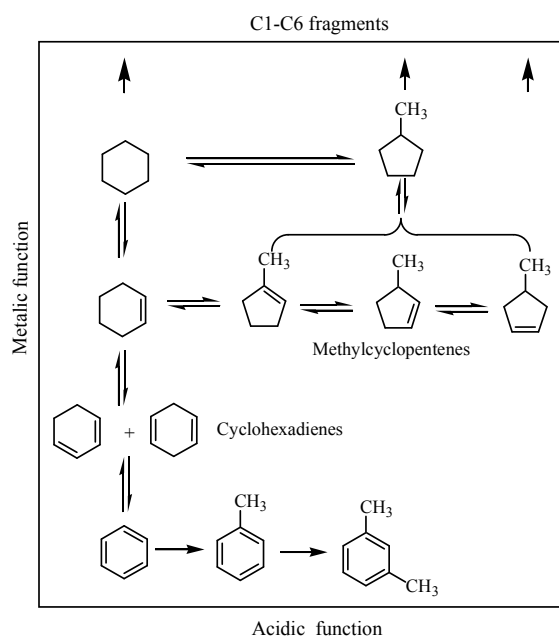


Fig. 7. Cyclohexadienes production using the PtRe/H-ZSM-5 catalysts.



Scheme 1. Proposed scheme for cyclohexene hydroconversion.

the maximum CHDE amounts were 2.1%, and 2.7% at 300 and 375 °C, respectively. With the PtRe/H-ZSM-5(HCl) catalyst, the CHDEs increased gradually with temperature up to 0.23% at 400 °C.

2.6 Further dehydrogenation

Dehydrogenation intermediates 1,3- and 1,4-CHDEs dehydrogenate further on Pt (111) to benzene. Su et al. [45] and Tsai et al. [46] found that CHE is converted to benzene on all Pt planes. Gland et al. [47] observed that CHE dehydrogenation on Pt (111) occur at some intermediate state before chemisorbed benzene is generated. CHDEs with different strengths of adsorption on the catalysts play a sig-

nificant role in producing the ultimate products. More strongly adsorbed CHDEs retard aromatic formation. Peck and Koel [48] have assumed that the chemisorption of CHDEs on Pt (111) is irreversible and the chemisorbed monolayer dehydrogenates to form benzene upon heating. In the present work, the CHDEs reached maximum values of 0.23%–2.66% in the product (Fig. 7), which means that the CHDEs do not all remain chemisorbed on the metal surface till completely dehydrogenated to benzene. Figure 8 shows that the PtRe/H-ZSM-5(HCl) catalyst gave significantly more dehydrogenation products than the untreated and HF treated catalysts, particularly at the higher temperatures. At 400 °C, the dehydrogenation products of CHE amounted to 21.46% using the chlorinated PtRe/H-ZSM-5 catalyst, while with the fluorinated catalyst, the total dehydrogenation products amounted to 9.78%. This can be attributed to the higher diffusion restriction in case of the HF treated PtRe/H-ZSM-5, due to fluoro-aluminium debris deposition in the zeolite channels.

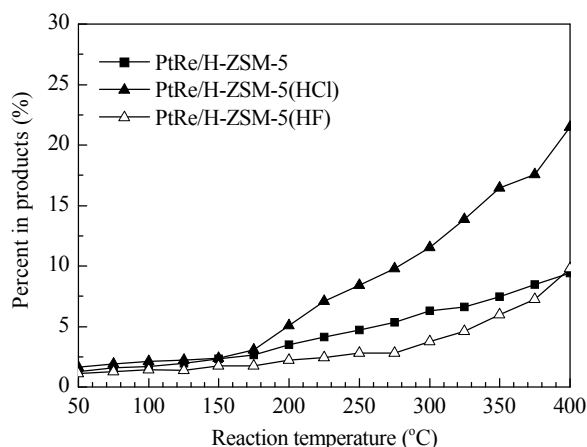


Fig. 8. Total dehydrogenation products using the PtRe/H-ZSM-5 catalysts.

2.7 Benzene production

Benzene is the most stable dehydrogenation product (final product), and hence a more active dehydrogenating catalyst will give a higher benzene production. Benzene production was low using the untreated and HF-treated catalysts (Fig. 9), and it was highest on the PtRe/H-ZSM-5(HCl) catalyst, it was ~2.0 at 50–150 °C and then increased continually beyond 150 °C to reach 15.3% at 400 °C. However, on the PtRe/H-ZSM-5 and PtRe/H-ZSM-5(HF) catalysts, benzene production increased slowly with temperature up to 400 °C. Benzene production on the catalysts was in the order of PtRe/H-ZSM-5(HCl) > PtRe/H-ZSM-5 ≥ PtRe/H-ZSM-5(HF). This is the order of acidic site strength distribution and PtRe dispersion in the catalysts.

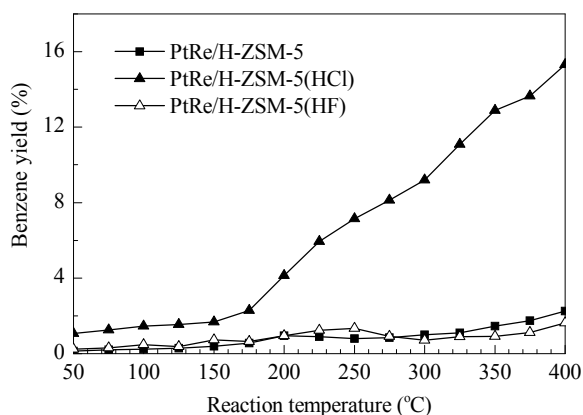


Fig. 9. Benzene yield using different catalysts.

2.8 Alkylated products

Benzene production was much higher on the PtRe/H-ZSM-5(HCl) catalyst (Fig. 9) than on the two other catalysts. However, toluene and xylenes (Figs. 10 and 11, respectively) were produced in lower quantities on this hydrochlorinated catalyst, indicating that more of the benzene

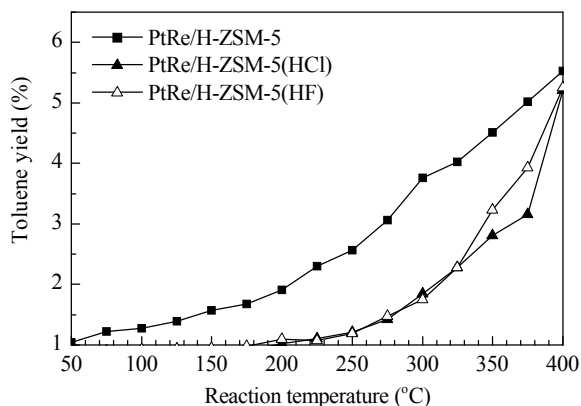


Fig. 10. Toluene in the product using the PtRe/H-ZSM-5 catalysts.

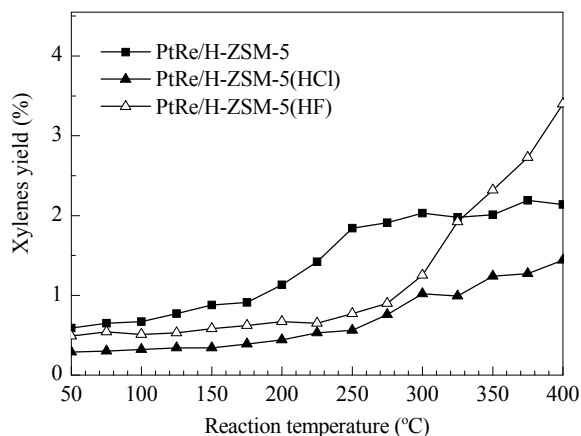


Fig. 11. Xylenes in the product using the PtRe/H-ZSM-5 catalysts.

was produced during the alkylation (by methyl groups produced through cyclohexene hydrogenolysis).

The production of toluene and xylenes by alkylation is normally dependent on catalyst acidity. Nevertheless, these alkylaromatics were produced in larger amounts on the unhydrohalogenated catalyst, PtRe/H-ZSM-5. The catalysts treated with HCl or HF possessed lower alkylation activities, although their acidities were higher. This can be attributed to the absence of chloro- and/or fluoro-alumino species deposited in the pores of the PtRe/H-ZSM-5 catalyst.

2.9 Hydrocracking reactions

Traditionally, the cracking of a probe compound (cumenene) is used to compare the strength of the acid sites in catalysts. However, in the present work, it is found that the bimetallic/zeolite catalyst (PtRe/H-ZSM-5) that was not treated with either HCl or HF gave the highest hydrocracking activity for cyclohexene. The catalysts were in the order of PtRe/H-ZSM-5 > PtRe/H-ZSM-5 (HF) > PtRe/H-ZSM-5(HCl) (Fig. 12). In contrast, unloaded H-ZSM-5 gave the following order of hydrocracking activities of H-ZSM-5(HF) > H-ZSM-5(HCl) > H-ZSM-5 [36], which is the same order of the acid site strength. This correlation showed that the bimetal combination, PtRe, which is a conventional metal combination in commercial industrial hydroisomerization catalysts, has a significant influence on inhibiting the hydrocracking activity of the catalysts. However, in our previous work [49] using a monometallic catalyst (Pt/H-ZSM-5), the same effect of hydrochlorination and hydrofluorination on the hydrocracking of cyclohexene was observed as Pt/H-ZSM-5 > Pt/H-ZSM-5(HF) > Pt/H-ZSM-5(HCl). This indicates that the addition of Re to Pt in H-ZSM-5 zeolite results in a significant alteration of the hydrocracking activity. It is to be noted that the inhibition of CHE hydrocracking by hydrohalogenation with HF or HCl (particularly HCl) is a favorable effect since this

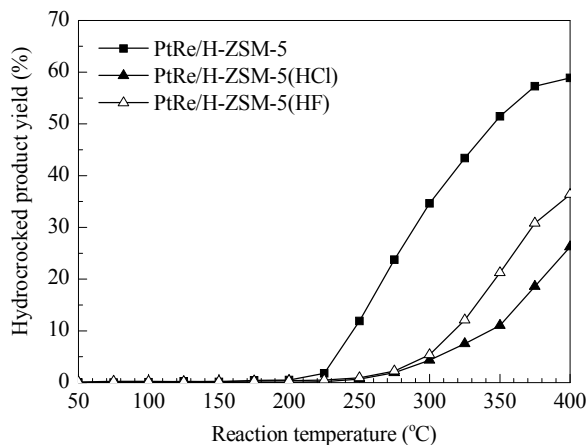


Fig. 12. Hydrocracked products using the PtRe/H-ZSM-5 catalysts.

reaction causes a loss of the valuable hydrocarbon feedstock.

3 Conclusions

The hydroconversion of CHE was excellent and was highest in the whole temperature range with PtRe/H-ZSM-5(HCl). At lower temperatures, ~90% of its activity was for the hydrogenation of CHE to CHA. The activity was the lowest on the untreated catalyst due to its lowest PtRe dispersion, and lowest number and strength of acid sites. Dehydrogenation activity was also the highest on the hydrochlorinated catalyst. The lowest hydrocracking activity was attained with the hydrochlorinated catalyst, while the highest was attained with the untreated catalyst. This study exhibited the advantage of the HCl treated catalyst since hydrocracking is a loss of the hydrocarbon reactant.

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