

Hydroconversion of cyclohexene using H-ZSM-5 zeolite catalysts promoted via hydrochlorination and/or platinum incorporation

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Abstract

Cyclohexene (CHE) was hydroconverted in a flow reactor at atmospheric pressure and temperatures of 50–400 °C using the catalysts: H-ZSM-5, H-ZSM-5(HCl), Pt/H-ZSM-5 or Pt/H-ZSM-5(HCl). The acid sites strength distribution, Pt dispersion, XRD, SEM and TEM photography for these catalysts were evaluated. The reaction steps of CHE hydroconversion were found to be as follows: CHE ↔ cyclohexane; CHE ↔ methylcyclopentenes (MCPEs) ↔ methylcyclopentane (MCPA); CHE ↔ cyclohexadienes (CHDEs) ↔ benzene; benzene ↔ alkylbenzenes; CHE and others ↔ hydrocracked products.

Doping of 3.0% HCl in H-ZSM-5 zeolite enhanced acid sites number and strength, whereas its doping in Pt/H-ZSM-5 enhanced acid sites number as well as Pt dispersion in the catalyst but slightly decreased the acid sites strength. The overall hydroconversion of CHE and its hydrogenation step to CHA were enhanced via incorporating Pt and/or doping with HCl. Also, CHE dehydrogenation was enhanced on the Pt/H-ZSM-5(HCl) catalyst, but was affected by diffusion limitation caused by deposited chloro-aluminium debris. The latter catalyst also suffered from diffusion effects during the acid catalysed alkylation and hydrocracking reactions. Indeed, HCl treatment, in the presence of Pt, significantly enhanced the debris lay-down and hence diffusion restriction. However, the isomerisation of CHE does not seem to depend on acid sites parameters or on Pt dispersion in the current catalysts. CHE dehydrogenation to benzene passes through the formation and removal of CHDEs. The magnitude of 1,3-CHDE in product using all catalysts exceeded that of 1,4-CHDE. Benzene formation was enhanced via HCl and/or Pt incorporation in the catalysts.

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1. Introduction

Cyclohexene (CHE) is frequently selected as a probe molecule for investigating catalyst preparation [1–4]. It undergoes various conversions depending on catalyst composition and the experimental conditions; temperature, presence or absence of hydrogen, and the pressure of hydrogen. In absence of hydrogen, disproportionation [5,6] and dehydrogenation [7,8] reactions take place. Disproportionation gives benzene and cyclohexane (CHA) and the reaction is termed hydrogen transfer when carried out in presence of metal catalysts, since CHE behaves as hydrogen donor and acceptor. If the metal is supported on

Al₂O₃ [9], the acid sites are of the weakly Lewis type, where the acid strength is not strong enough to promote carbonium ion formation, and hence isomerization and cracking reactions cannot occur. However, the H-forms of zeolites possess strongly acidic Brönsted and Lewis sites that promote CHE isomerization to a mixture of MCPEs and cracking to lower molecular weight compounds whereby the reaction scheme becomes more complicated. However, treatment of the cation-exchanged zeolites with aqueous HCl acid leads to decationation and partial dealumination.

The results of isomerization of CHE over highly pure aluminas with or without Cl[−] ions has been studied by Ozimek et al. [10,11]. Introducing Cl[−] ions into aluminate aluminas in different ways causes Brönsted acid sites to appear and a drastic increase of both skeletal isomerization and total conversion. The promoting effect of adsorbed Cl[−] ions on the surface acid-

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ity of γ -Al₂O₃ has been monitored by zero point charge (z.p.c.) and CHE isomerization activity [12] showing a linear progressive decrease of the z.p.c. values with increasing the extent of chloride adsorption. The thermal stability of the γ -Al₂O₃(Cl) has been investigated via dechlorination tests and surface area measurements. Surface dehydroxylation causes Cl⁻ loss and surface area decay. Steam markedly enhances the dechlorination rate.

CHE hydrogenation and dehydrogenation are much faster than benzene hydrogenation and CHA dehydrogenation, respectively, particularly, using noble metal catalysts. Recently, Aboul-Gheit and co-workers have studied aromatics hydrogenation [13], hydroconversion of *n*-paraffins in light naphtha [14], CHA 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) as well as with Cl⁻ or F⁻. Again, CHE hydrogenation and/or dehydrogenation have been investigated using Ni, Pt, Rh and Pd catalysts [17–26]. CHE hydroconversion over catalysts containing 0.35 wt.% of the monometals Rh, Pt, Ir, Re or U and bimetals PtRh, PtIr, PtRe or PtU on γ -Al₂O₃ was carried out in a pulsed microreactor at temperatures of 50–250 °C [9]. The effect of doping with 3.0 wt.% of Cl⁻ or F⁻ was examined. The bimetallic combinations on alumina give more active catalysts than the monometallic catalysts. The activities of all monometallic catalysts were significantly enhanced by Cl⁻ incorporation.

The effect of Cl⁻ ions added, either as a part of the Pt precursor or after the noble metal impregnation, on the catalytic activity of Pt/Al₂O₃ for complete oxidation of toluene, has been studied [27]. An inhibitory effect of chlorine has been proved and assigned to the formation of oxychlorided platinum species. Nevertheless, a highly dispersed 1.0 wt.% Ir/Al₂O₃ catalyst with 1.0 wt.% Cl, as well as its counterparts with <0.2% Cl, with or without sintering, were tested in *n*-hexane reactions at 453–603 K [28]. The Cl⁻ containing catalyst was considerably less active in this temperature range (unfavorable for bifunctional reactions).

In the present work, unloaded H-ZSM-5 and Pt loaded H-ZSM-5 catalysts have been doped with 3.0 wt.% HCl to visualize this effect on CHE hydroconversion in a flow reactor operated in a flow of hydrogen at temperatures of 50–400 °C.

2. Experimental

2.1. Preparation of the catalysts

2.1.1. H-ZSM-5 catalyst

This catalyst was prepared via exchanging Na-ZSM-5 zeolite with 0.6 M NH₄NO₃ solution followed by drying at 110 °C overnight and calcination for 4 h at 550 °C. The mother Na-zeolite was kindly provided by the Süd Chemie, München, Germany. The H-form (H-ZSM-5) acquired a Si/Al ratio of 23.8, a surface area of 440 m² g⁻¹, a pore volume of 0.16 cm³ g⁻¹ and a sodium content <0.002%.

2.1.2. H-ZSM-5(HCl) catalyst

A part of the mother zeolite prepared in Section 2.1.1 was doped with a solution of hydrochloric acid containing the requisite quantity for 3.0 wt.% HCl, dried then calcined as above.

2.1.3. Pt/H-ZSM-5 catalyst

A part of the mother zeolite, prepared in Section 2.1.1 was impregnated with a solution containing the requisite quantity of H₂PtCl₆ to contain 0.35 wt.% Pt. The catalyst was dried and calcined as above, then reduced at 500 °C for 8 h in the reactor using pure hydrogen gas flow.

2.1.4. Pt/H-ZSM-5(HCl) catalyst

A part of the catalyst prepared in Section 2.1.3 was doped with HCl solution sufficient to contain 3.0 wt.% HCl, dried, calcined then reduced as above.

All catalysts prepared in Sections 2.1.1–2.1.4 retained the majority of the crystallinity originally acquired by the H-ZSM-5 zeolite prepared in Section 2.1.1 as revealed by X-ray diffraction analysis, where the 100% diffraction peak in all forms appeared at 2θ of 23.0°. However, a very slight increase of the diffraction peak at 2θ of 10.88369° in the XRD diffraction patterns of both H-ZSM-5(HCl) and Pt/H-ZSM-5(HCl) catalysts indicated very low bulk dealumination of the H-ZSM-5 zeolite.

2.2. Hydroconversion reactor system and reaction product analysis

A silica-glass flow reactor tube containing 0.2 g of a catalyst was used in carrying out the hydroconversion runs. The reactor was heated in an insulated wider silica tube jacket, thermostated to ± 1 °C. Hydrogen gas was used as a carrier and simultaneously as a reactant in the current reaction at a flow rate of 20 cm³ min⁻¹ in all runs. The feed (CHE) was introduced into the reactor via continuous evaporation using the carrier flow passing into a closed jar thermostated at a fixed temperature of 28 °C whereby the quantity of cyclohexene was always 8.33×10^{-3} mol h⁻¹; i.e. the H₂/CHE ratio was 6.4 in all runs. The amount of CHE condensed between saturator and reactor was always considered in calculating the actual weight of CHE flowing to the catalyst. The reaction temperatures investigated were 50–400 °C, with 25 °C decrements starting from 400 °C downwards. The gaseous reaction effluent passing from the reactor was injected in a Perkin-Elmer Autosystem XL gas-chromatograph using a 15 m capillary column of Carbowax 20 M bonded in fused silica to be analysed, FID detector and a Turbochrom Navigator Programme. This GC column system separated the product effluent to: hydrocracked components, MCPEs, MCPA, CHE, CHA, CHDEs (1,3- and 1,4-) and aromatics (benzene, toluene and xylenes). Examination of the metal free H-ZSM-5 zeolites, H-ZSM-5 and H-ZSM-5(HCl), for CHE hydroconversion for time-on-stream of 180 min at 400 °C did not show any decrease of the catalysts activities. Moreover, examination of these catalysts for carbon deposition using temperature-programmed oxidation in a differential scanning calorimetry (DSC) unit did not show the CO₂ peak.

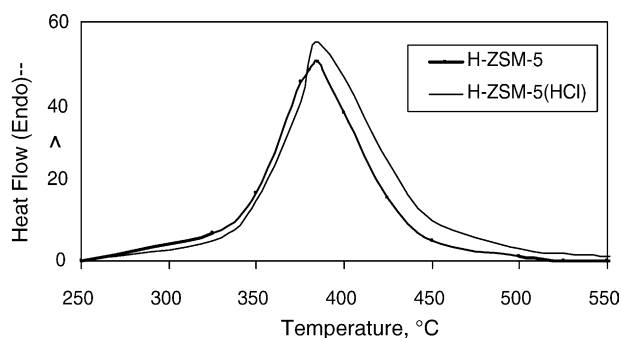


Fig. 1. Temperature-programmed desorption of NH_3 from strong acid sites of H-ZSM-5 zeolites.

2.3. Temperature-programmed desorption (TPD) of ammonia

The procedure adopted by Aboul-Gheit [29,30] using differential scanning calorimetry (DSC) for detecting the desorption of presorbed ammonia from a catalyst was applied. Primarily, NH_3 gas was chemisorbed on the catalyst sample in a silica tube furnace after evacuation at 1.33×10^{-3} Pa whilst heating at 500°C . Subsequent cooling under vacuum to 50°C was performed and NH_3 was introduced through the catalyst bed at a flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$. Desorption of NH_3 from the catalyst was rapidly measured in a DSC unit (Mettler TA-3000) using standard Al crucibles in nitrogen purge gas flowing at a rate of $30 \text{ cm}^3 \text{ min}^{-1}$. The heating rate was 10 K min^{-1} and the full-scale range was 25 mW.

Fig. 1 shows the NH_3 TPD thermograms for the unloaded H-ZSM-5 and H-ZSM-5(HCl) zeolites during the high DSC temperature range ($250\text{--}600^\circ\text{C}$). Indeed, normally two endothermic peaks appeared in the experimental thermograms, but we did not show in Fig. 1 the low temperature peak ($\sim 50\text{--}250^\circ\text{C}$) which represents NH_3 desorption from the weak acid sites in the zeolites, since these weak sites do not participate in the current catalytic reactions. It is to be noticed that the Pt/H-ZSM-5 and Pt/H-ZSM-5(HCl) versions, when examined for NH_3 TPD, also show thermograms similar to those in Fig. 1, but with somewhat varying desorption properties; i.e. with lower NH_3 desorption enthalpy and lower peak temperature (Table 1). The NH_3 desorption enthalpy was taken to correlate the number of strong acid sites, whereas the peak temperature was taken to correlate the strength of these acid sites.

2.4. Surface area and dispersion of platinum in the catalysts

The dispersion of Pt in the catalysts (fraction of metal exposed) was determined by hydrogen chemisorption using a pulse technique similar to that described by Freel [31]. A calcined catalyst was heated in the chemisorption furnace at 500°C for 3 h in a flow of $50 \text{ cm}^3 \text{ min}^{-1}$ of ultra-pure hydrogen. The flow was then replaced with oxygen-free nitrogen gas for 2 h at a flow rate of $30 \text{ cm}^3 \text{ min}^{-1}$ at 500°C (degassing). The furnace was shut off and catalyst was cooled to room temperature. Hydrogen was then pulsed into the nitrogen carrier gas till saturation, i.e. till appearance of hydrogen peaks equivalent to complete volumes of unchemisorbed pulses. The hydrogen uptake was calculated as hydrogen atoms chemisorbed per total Pt atoms. The surface area of the metal was also calculated, based on an area of one H_2 molecule of $12 \times 10^{-16} \text{ m}^2$. Platinum dispersion and surface area are given in Table 1.

2.5. X-ray diffraction patterns of the catalysts

The X-ray diffraction patterns of the catalysts under study were carried out using a Phillips X'Pert Diffractometer PW 1390 at 40 kV and 30 mA with Ni Filter and Cu $\text{K}\alpha$ radiation. The XRD runs were carried out up to 2θ of 60° .

The traditional XRD patterns obtained for the current catalysts whether loaded with Pt or unloaded (not given) show more or less similar intensities of the diffraction peaks. The 100% crystallinity peak appeared in all samples at 2θ of 23.0° . Moreover, the HCl doped samples show slightly higher relative intensity of the lowest 2θ peak, due to slight dealumination of the zeolite.

2.6. Scanning and transmission electron microscopy (SEM and TEM)

The SEM samples were mounted on Al slabs and sputter-coated with a thin gold layer of $\sim 150 \text{ \AA}$ thickness using an Edward sputter-coater. The samples were then examined in an SEM model JXA-890 Electron Probe microanalyzer (JEOL) at 30 kV.

For TEM examination, one drop of the suspension of the powdered sample in distilled water was mounted on a copper grid, primarily coated with a carbon film, then left to dry and examined using TEM model EM10 ZEISS at 60 kV.

Table 1
Ammonia TPD and H_2 chemisorption data for Pt surface area and dispersion in the catalysts

Catalysts	Acid sites strength distribution		H_2 chemisorption on Pt in the catalysts	
	ΔH_d (J g^{-1}) ^a	Peak temperature ($^\circ\text{C}$) ^b	Pt surface area ($\text{m}^2 \text{ g}^{-1}$)	Pt dispersion (%)
H-ZSM-5	98.4	380.1	–	–
H-ZSM-5(HCl)	108.5	384.4	–	–
Pt/H-ZSM-5	88.8	376.2	0.94	72.4
Pt/H-ZSM-5(HCl)	91.9	374.9	1.11	85.7

^a Proportional to acid sites number.

^b Proportional to acid sites strength.

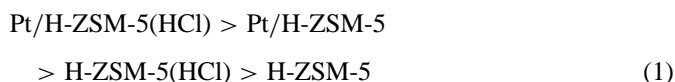
3. Results and discussion

Injection of light organic chlorohydrocarbons in the light-naphtha hydroisomerisation reactor is almost normally practiced for chlorinating the conventional commercial Pt/Al₂O₃ catalysts. These chlorohydrocarbons are converted to HCl and small hydrocarbons. The HCl gas formed is necessary for redistributing the platinum crystallites and inhibits their growth to agglomerates, as well as to enhance the acidity of these catalysts. This treatment may differ from what is normally applicable in preparing the chlorinated Pt/H-ZSM-5 catalysts, where the support is first halogenated before impregnating or exchanging with a Pt precursor, followed by drying, calcination and reduction.

However, in the present work, calcined H-ZSM-5 and Pt/H-ZSM-5 catalysts have been doped with 3.0 wt.% HCl acid solution then recalcined and reduced, and tested for CHE hydroconversion at reaction temperatures ranging between 50 and 400 °C. This treatment is aimed to visualise the effect of post-hydrochlorination of the zeolite containing catalysts either unloaded or loaded with Pt although it is generally reputed that H-forms of zeolites possess sufficient strong acid sites which make them not requiring such post-hydrochlorination. The present investigation clarifies how far this HCl treatment produces significant catalytic activity enhancement, particularly, for the hydrogenation and dehydrogenation steps.

3.1. Hydroconversion of cyclohexene

The changes resulting on the CHE hydroconversion activities of the catalysts containing 0.35 wt.% Pt supported on H-ZSM-5 after treatment with 3.0 wt.% HCl, compared to those using the corresponding unloaded zeolite are depicted in Fig. 4. Evidently, HCl doping has enhanced the overall hydroconversion activities of both unloaded and Pt loaded H-ZSM-5 zeolite containing catalysts, such that the activities of the current catalysts can be arranged in the order:



The effect of Pt-loading on the zeolite is obvious during the lower temperature range up to, cf. 300 °C compared to the corresponding unloaded zeolite catalysts. Beyond 300 °C, the activities of the four current catalysts do not exhibit marked differences, although the HCl doped catalysts show somewhat lower activities than the respective unchlorinated versions which may be attributed to some diffusion limitation due to few debris particles of chloro-aluminium species. So, for instance, at 350 °C, CHE hydroconversion amounts to 85.3 and 93.3% using the H-ZSM-5(HCl) and H-ZSM-5 catalysts, respectively, and 95.4 and 97.3% using the Pt/H-ZSM-5(HCl) and Pt/H-ZSM-5 catalysts, respectively. The influence of diffusion limitation is known to act more obviously at the high temperature region.

On the contrary, the activities during the lower temperature range (<300 °C) are directly following order (1) given above. So,

for instance, at 50 °C, using the H-ZSM-5(HCl) and H-ZSM-5 catalysts, CHE hydroconversion amounts to 8.1 and 2.2%, respectively, and at 150 °C amounts to 15.7 and 4.2%, respectively. In comparison, using the Pt/H-ZSM-5(HCl) and Pt/H-ZSM-5 catalysts, at 50 °C, CHE hydroconversion amounts to 59.6 and 20.2%, respectively, and 90.7 and 66.0%, respectively, at a temperature of 150 °C. Evidently, at the lower temperature range, there is no effective diffusion restrictions.

The significant enhancement of CHE hydroconversion at temperatures <300 °C, resulting via HCl doping in the unloaded H-ZSM-5 zeolite is attributed to increasing the acid sites number and strength (Table 1). This table shows that the desorption enthalpy (ΔH_d) enhancement of adsorbed ammonia on the acid sites of H-ZSM-5 zeolite, due to 3.0% HCl incorporation, increases from 98.4 to 108.5 J g⁻¹ (ΔH_d is proportional to acid sites number) since the heat (enthalpy) required for desorbing a number of ammonia molecules increases with increasing this number and vice versa. Also, the ammonia desorption peak temperature is proportional to acid sites strength, since stronger acid sites which adsorb ammonia molecules require higher temperatures to desorb them than to desorb ammonia molecules from weaker acid sites. Doping of HCl in H-ZSM-5 zeolite causes the ammonia desorption peak to shift from 380.1 to 384.4 °C. However, the enhancement observed for CHE hydroconversion using the Pt/H-ZSM-5 catalyst via similar HCl incorporation can be attributed to: (a) increasing the dispersion of Pt and its surface area in the zeolite; as well as to (b) increasing the acid sites number. Table 1 also shows that the ΔH_d value for ammonia desorption from the acid sites of the Pt/H-ZSM-5 catalyst increases from 88.8 to 91.9 J g⁻¹ but the ammonia desorption peak temperature slightly decreases from 376.2 to 374.9 °C via incorporating 3.0% HCl. The dispersion of Pt and its surface area in Pt/H-ZSM-5 amount to 72.4% and 0.94 m² g⁻¹, respectively, whereas for the Pt/H-ZSM-5(HCl) catalyst these values increase to 85.7% and 1.11 m² g⁻¹, respectively.

Fig. 2a and b show the SEM micrographs for the Pt/H-ZSM-5 and Pt/H-ZSM-5(HCl) catalysts, respectively, at a magnification of 4300 times. Evidently, HCl incorporation in the catalyst has caused the Pt crystallites to become smaller and hence, the catalyst activity increased. The TEM micrographs obtained for the same catalysts are shown in Fig. 3a and b, respectively. These micrographs seem to substantiate the SEM results, where redistribution of the Pt crystallites has produced a large quantity (~60%) of smaller particles (considering magnification difference; 40,000 in Fig. 3a and 50,000 in Fig. 3b).

3.2. Hydrogenation of cyclohexene to cyclohexane

An unsaturated hydrocarbon molecule such as CHE, in the initial adsorption process interacts largely through the most energetically favourable donor π and acceptor π^* orbitals with appropriate metal surface orbitals. Hence, on an atomically flat surface, CHE can form a chemisorption state in which the C₆ ring would lie largely 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 cyclohexane (CHA). Fig. 5 shows that the HCl treated versions of

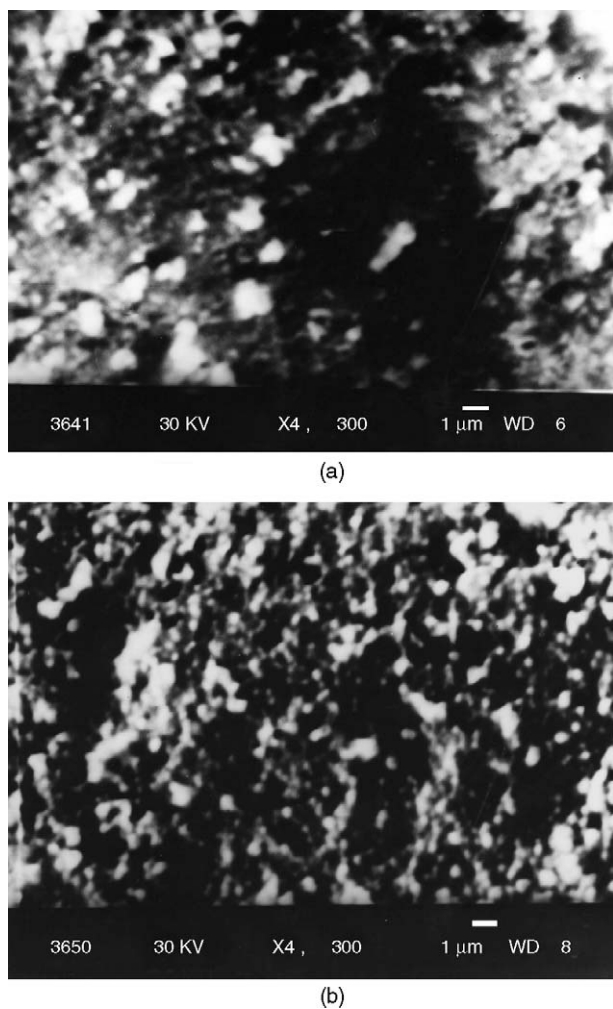


Fig. 2. SEM for: (a) Pt/H-ZSM-5 catalyst and (b) Pt/H-ZSM-5(HCl) catalyst.

catalysts, whether loaded with Pt or unloaded, are more active than their untreated versions, and that the Pt loaded catalysts are significantly more active than the Pt-free catalysts. For instance, using the HCl treated Pt/H-ZSM-5 catalyst, CHA comprises as high as 58.6% of product at as low a temperature as 50 °C then actively rises to a maximum of 86.8% at 150 °C. However, the untreated Pt/H-ZSM-5 catalyst gives a much lower CHA yield (19.3%) at 50 °C and rises to reach a maximum of 63.0% at 175 °C. This can be attributed, as mentioned above, to a significant improvement of the dispersion and surface area of Pt via HCl treatment. The Pt sites are primarily responsible for CHE hydrogenation reactions [32] at low reaction temperatures (50–150 °C), whereas the Brönsted acid sites in the unloaded zeolite are responsible for CHE hydrogenation at relatively higher temperatures than hydrogenation on the metallic sites. However, enhancement of the hydrogenation activity of the unloaded H-ZSM-5 zeolite via HCl treatment can be attributed to creation of stronger Brönsted acid sites. Sano et al. [33] show that 95% of ethylene hydrogenates to ethane at a temperature of 535 °C using H-ZSM-5 zeolite as a catalyst. Also, Kanai et al. [34] assume that Brönsted acid sites become active hydrogenation–dehydrogenation sites for alkenes at higher temperatures. Moreover, Senger and Radom [35] have stated that the

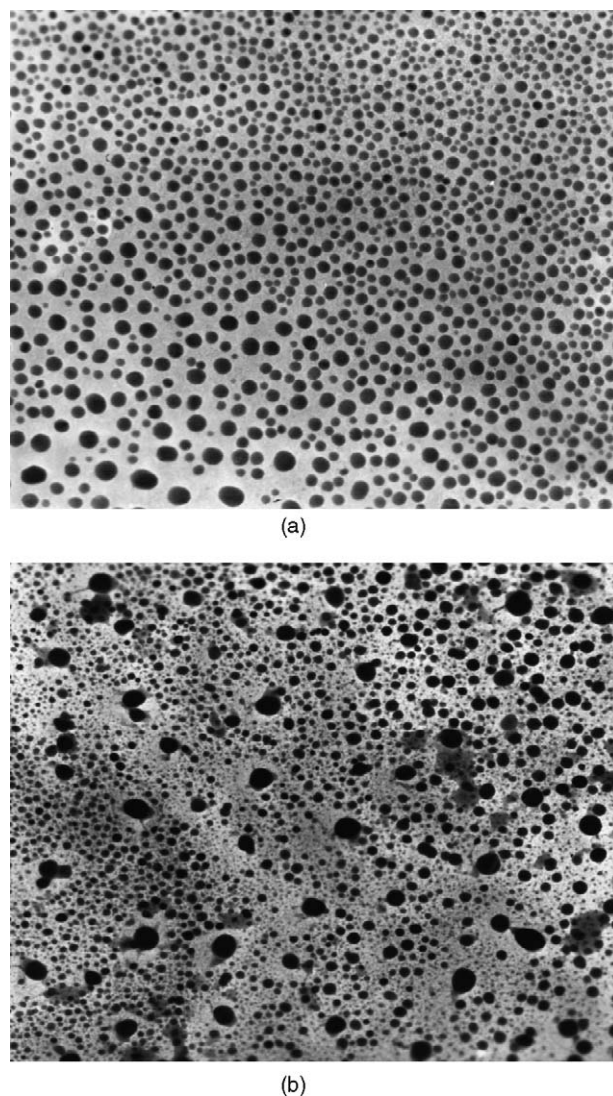


Fig. 3. TEM for: (a) Pt/H-ZSM-5 catalyst (magnification: 40,000×) and (b) Pt/H-ZSM-5(HCl) catalyst (magnification: 50,000×).

Brönsted acid sites become active centers for the hydrogenation of olefinic bonds.

Fig. 5 shows that maximum hydrogenation of CHE on the unloaded H-ZSM-5 and H-ZSM-5(HCl) catalysts is accomplished at 300 °C and amounts to almost equal values of ~13.5%, it is evident that during the 50–250 °C temperature range, the HCl treated zeolite catalyst attains higher activity than the untreated one (Fig. 5). For instance, at 200 °C, CHA is only 1.4% using the H-ZSM-5 catalyst but rises to 9.0% on the H-ZSM-5(HCl) catalyst.

3.3. Isomerisation of cyclohexene to methylcyclopentenes (MCPEs)

The data in Fig. 6 depict the change in the percentages of methylcyclopentenes (MCPEs) mixtures in product as a function of reaction temperature using the catalysts under study. As reaction intermediates, these isomers (MCPEs) increase with increasing reaction temperature to reach a maximum, beyond

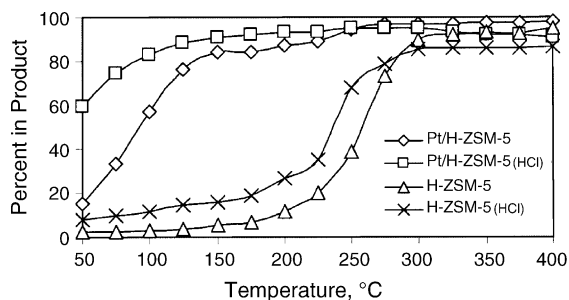
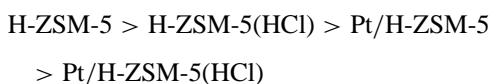


Fig. 4. Hydroconversion of CHE using HCl and/or Pt promoted H-ZSM-5 catalysts.

which they decrease with a further increase of temperature. The maxima of these isomers in product can be arranged in the catalysts order as follows:



This order is the reverse of the orders of hydroconversion activities of the current catalysts (Fig. 4) and their hydrogenation activities (Fig. 5). In other words, the yield of these MCPEs is higher in the product using a less active hydrogenation catalyst. Since these products are unsaturated isomers of CHE, they are subject to be saturated to MCPA under reaction conditions, hence the more active hydrogenating catalysts will produce lower MCPEs (Fig. 6) and higher MCPA (Fig. 7).

The overall isomerisation activity of any of the current catalysts can be assumed to be the sum of unsaturated and saturated C₅-ring containing compounds; i.e. MCPEs + MCPA (Fig. 8). This assumption has been treated in a quasi-mathematical form by Dwyer et al. [36] who defined the relative rates of isomerisation (monomolecular reaction) and bimolecular hydrogen transfer as follows:

$$\frac{\text{isomerisation}}{\text{hydrogen transfer}} = \frac{I(\text{MCPEs} + \text{MCPA})}{I(\text{CHA} + \text{MCPA})}$$

where *I* refers to the initial selectivities. Tjandra and Zaera [37] and Jolly et al. [38] also substantiate Dwyer et al. assumption. During the low temperature range (50–150 °C), the sum of iso-

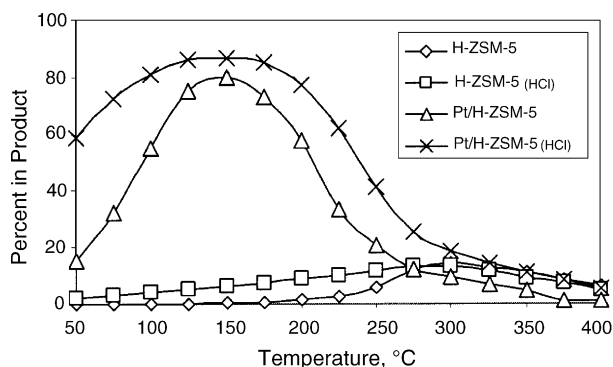


Fig. 5. Hydrogenation of CHE to CHA using HCl and/or Pt promoted H-ZSM-5 zeolite catalysts.

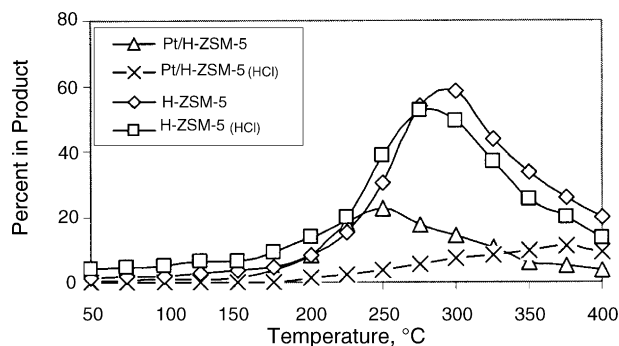


Fig. 6. MCPEs in product using HCl and/or Pt promoted H-ZSM-5 zeolite catalysts.

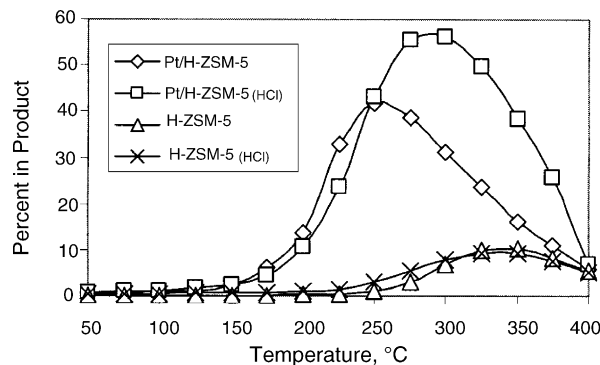


Fig. 7. MCPA in product using HCl and/or Pt promoted H-ZSM-5 catalysts.

mers is highest on the H-ZSM-5(HCl) catalyst; for instance, at 125 °C this sum amounts to 7.0% on this catalyst compared to as low as 1.6–2.8% on the three other catalysts under study. This can be attributed to acquiring the highest acid sites number and strength by this H-ZSM-5(HCl) catalyst compared to the three other current catalysts as shown in Table 1. However, at high temperatures, the maximum overall isomers levels using the Pt/H-ZSM-5, Pt/H-ZSM-5(HCl) and H-ZSM-5 catalysts are not significantly different, i.e. 64.6 (at 250 °C), 63.5 (at 300 °C) and 65.3% (at 300 °C), respectively. This indicates that the maximum isomerisation level from the six-membered ring to the five-membered one is not such critical with respect to the catalyst specifications, however, the rate of this reaction is

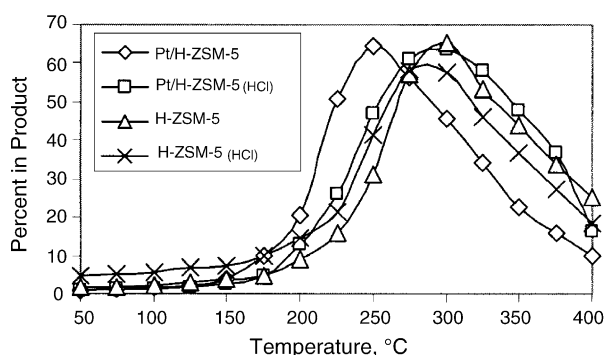
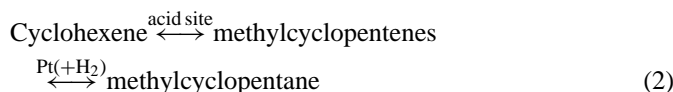


Fig. 8. Overall hydroisomerisation of CHE using HCl and/or Pt on H-ZSM-5 catalysts.

higher using the Pt/H-ZSM-5 catalyst (higher at lower temperatures). The absence of HCl in this catalyst, although decreases its acid strength, it increases the number of its acid sites and most importantly rescues the catalyst against depositing amorphous chloro-aluminium debris in its pores.

The reaction sequence in Eq. (2) shows that a molecule of CHE rearranges on an acid site producing an equilibrium mixture of MCPEs, which hydrogenate with a molecule of hydrogen on a Pt site producing a MCPA molecule.



3.4. Hydrogenation of methylcyclopentenenes to methylcyclopentane

Evidently, the hydrogenation of MCPEs to MCPA takes place at significantly higher temperatures (Fig. 7) than the hydrogenation of CHE to CHA (Fig. 5). Using the Pt/H-ZSM-5 and Pt/H-ZSM-5(HCl) catalysts, maximum hydrogenation of CHE to CHA is 63.2 and 86.8%, respectively, at temperatures of 175 and 150 °C, respectively, whereas the hydrogenation of the C₅-ring alkenes (MCPEs) to MCPA amounts to 41.9 and 56.3%, respectively, at temperatures of 250 and 300 °C, respectively. The higher temperatures required for hydrogenating the five-membered ring cycloalkenes than those required for hydrogenating the six-membered ring cycloalkenes have been attributed by Balandin [39] to the more restricted orientation, adsorption and hydrogenation of the C₅-ring on the catalyst surface. Balandin assumes an edgewise adsorption of the five-membered ring, whereas the cyclohexene ring adsorption takes place directly flat (planar) on the catalyst surface. Aboul-Gheit [40] found that the entropy of activation for hydrogenating indole (five-membered ring nitrogen compound) is much lower than that for the six-membered ring compound (quinoline), indicating a loss of significant freedom degrees during hydrogenating the C₅ ring compound. The efficiency order of the current catalysts, for the hydrogenation of MCPEs to MCPA (Fig. 7) is compatible with that found for hydrogenating CHE to CHA (Fig. 5) (order (1)). This compatibility of the orders of catalytic efficiencies and the magnitude of temperatures at which the reactions take place may indicate that both hydrogenations take place on the same type of hydrogenation sites; i.e. using the Pt/H-ZSM-5(HCl) and Pt/H-ZSM-5 catalysts, the Pt sites act as hydrogenation sites, whereas using the H-ZSM-5(HCl) and H-ZSM-5 catalysts, the Brønsted acid sites act as hydrogenation sites, as has been emphasised by above-mentioned investigators [33–35].

It can be decided that MCPA is formed only via hydrogenation of MCPEs and not via a backward isomerisation of CHA. This can be evidenced via comparing the order of the catalysts activities for producing MCPEs in Fig. 6 and MCPA in Fig. 7. It is known that the isomerisation of an olefin to another olefinic isomer(s) takes place straightforward, whereas isomerisation of a paraffinic molecule to an isoparaffin requires, first, to be dehydrogenated to the olefin.

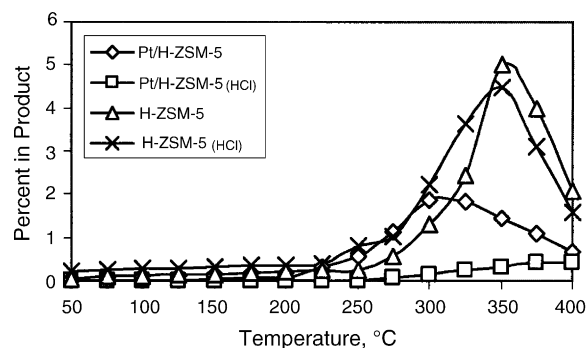
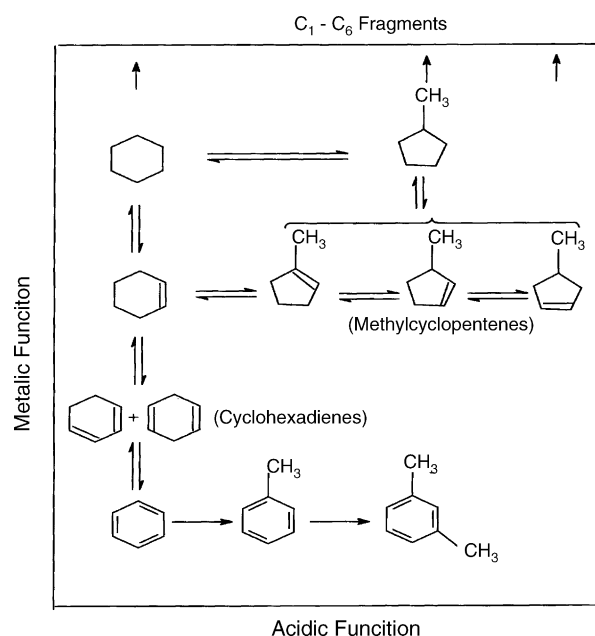


Fig. 9. CHDEs in product using HCl and/or Pt promoted on H-ZSM-5 zeolite catalysts.

3.5. Dehydrogenation of cyclohexene to cyclohexadienes

CHE is primarily dehydrogenated to a mixture of 1,3- and 1,4-cyclohexadienes (CHDEs). These cyclic dienes are further dehydrogenated at a high rate as observed from their low concentrations in the product (Figs. 9 and 10). Land et al. [41] assume that CHE at low temperatures is bonded to the Pt substrate in a di- σ fashion, similar to what is known for ethylene [42]. The di- σ bonded CHE may undergo conversion analogous to olefin metathesis to form the bis (alkylidene), 1,6-hexadialkylidene. Further, CHDEs are converted to benzene which is the most stable dehydrogenation product. These two dehydrogenation steps (Scheme 1), increase with reaction temperature because of their endothermicity.

Fig. 9 shows that the sum of 1,3- and 1,4-CHDEs increases with reaction temperature over the current catalysts. Using the untreated Pt/H-ZSM-5 catalyst, maximum CHDEs amount to 1.9% at 300 °C, whereas using the Pt/H-ZSM-5(HCl) catalyst, this maximum is as low as 0.44% at 400 °C. However, using



Scheme 1. Proposed scheme for pathways of cyclohexene hydroconversion using the current bifunctional catalysts.

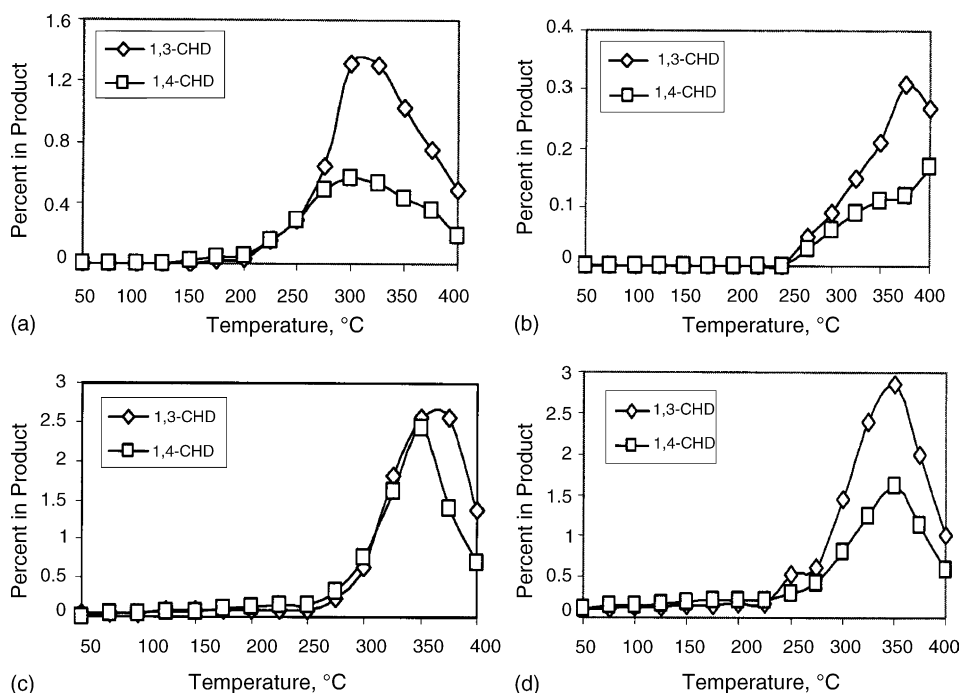
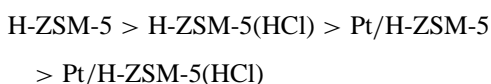


Fig. 10. Individual CHDEs in product using: (a) Pt/H-ZSM-5 catalyst; (b) Pt/H-ZSM-5(HCl) catalyst; (c) H-ZSM-5 catalyst; (d) H-ZSM-5(HCl) catalyst.

the unloaded H-ZSM-5 and H-ZSM-5(HCl) catalysts, maximum CHDEs comprise 5.0 and 4.5%, respectively, at 350 °C. Hence, maximum CHDEs in the product using the current catalysts can be arranged in the following order:



Evidently, this order of catalysts activities towards CHE dehydrogenation to CHDEs, reflects the reverse order of the true catalysts activities towards CHE hydroconversion and hydrogenation where: Pt/H-ZSM-5(HCl) > Pt/H-ZSM-5 > H-ZSM-5(HCl) > H-ZSM-5. Hence, it can be assumed that, the higher the fraction of CHDEs which remains unconverted in the reaction product, the slower is the rate of completing the dehydrogenation cycle to benzene on these catalysts (3).



Fig. 10a–d shows the magnitude of the individual intermediates (1,3- and 1,4-CHDEs) in the product using the current catalysts as a function of reaction temperature. Evidently, 1,3-CHDE is always higher than the 1,4-isomer, which may indicate that 1,3-CHDE is easier to be formed than the 1,4-isomer, and/or that the latter is more rapidly converted to benzene. Using the untreated Pt/H-ZSM-5 catalyst (Fig. 10a), both isomers are almost of equal concentrations in the product up to a temperature of 250 °C, beyond which the 1,3-isomer largely exceeds the 1,4-isomer. Both isomers increase with a further increase of the temperature to reach maxima of 1.30 and 0.56%, respectively, at a temperature of 300 °C. On the contrary, using the HCl treated catalyst (Pt/H-ZSM-5(HCl)) (Fig. 10b), the values

of 1,3- and 1,4-CHDEs comprise the lowest values obtained; i.e., the 1,3-isomer attains a maximum of 0.30% at 375 °C, whereas the 1,4-isomer continually increases to reach 0.17% at 400 °C. Somorjai and co-workers [43] have concluded that hydrogenation was the only detectable reaction at temperatures of 27–127 °C with 1,3-CHDE on the surface as revealed by *sum frequency generation*. A further increase of temperature results in a decrease in the hydrogenation rate and an increase in the dehydrogenation rate with both 1,3- and 1,4-CHDEs detectable on the surface simultaneously. The following mechanism was then postulated by these authors; CHE hydrogenates to CHA via 1,3-CHDE intermediate, and dehydrogenates to benzene through both 1,3- and 1,4-CHDE intermediates on Pt(1 1 1).

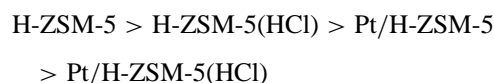
In a trial to correlate our data, with those of Somorjai and co-workers [43], we have calculated the ratio of 1,4-/1,3-CHDEs at low temperatures (very low values which are not visible in the curves) range between 2.5 at 150 °C and 0.35 at 300–400 °C; i.e. 1,4-CHDE is the most predominant isomer at lower temperatures, then decreases relative to 1,3-CHDE with increasing temperature; i.e. 1,3-CHDE increases during the CHE dehydrogenation region. Hence, this finding is evidently contradicting with that of Somorjai's using Pt(1 1 1) catalyst and SFG analysis. It can be assumed that the catalytic functions and operating conditions have the principal role directing the hydrogenation–dehydrogenation mechanism. Again, it is also found that HCl treatment of our Pt/H-ZSM-5 catalyst may make the mechanism operate differently at the high temperature range (275–400 °C) where dehydrogenation prevails and the 1,4-/1,3-CHDEs ratio is ~0.5; i.e. the 1,3-isomer is approximately twice the 1,4-isomer. Anyhow, the absence of quantitative data for the CHDE isomers during the temperature ranges investigated in Somorjai's and co-workers [43] work does not allow us to

have strict correlations with their mechanism. However, using the unloaded H-ZSM-5 and H-ZSM-5(HCl) catalysts (Fig. 10c and d, respectively) another view of the isomers concentrations appears. On the former catalyst, the 1,4-/1,3-CHDEs ratio is close to unity at as high as 350 °C (during the optimum dehydrogenation region). These data may correlate somewhat closer to those of Somorjai and co-workers [43], but our catalysts in Fig. 10b and c do not contain Pt for a justifiable correlation.

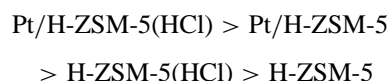
3.6. Dehydrogenation of CHDEs to benzene

Passing through dehydrogenation to the intermediates 1,3- and 1,4-CHDEs, Somorjai and co-workers [43] find that CHE dehydrogenates on Pt(1 1 1) catalysts further to benzene; a reaction which is typically endothermic. Also, Tsai et al. [44] find that CHE is converted to benzene on all Pt planes. Gland et al. [45] observe that CHE dehydrogenation on Pt(1 1 1) must occur at some intermediate state before chemisorbed benzene is generated. CHDEs possess different strengths of adsorption on the catalysts that play a significant role in producing the ultimate products. Stronger adsorption of CHDEs appears to retard aromatics production. Peck and Koel [46] have assumed that chemisorption of CHDEs on Pt(1 1 1) is irreversible and all chemisorbed monolayer dehydrogenates to form benzene upon heating. In the present work, CHDEs are found in percentages approaching 2.5% in product using the Pt/H-ZSM-5 catalyst (Fig. 10c), which does not mean that CHDEs remain chemisorbed on Pt surface till completely dehydrogenated to benzene. However, supporting Pt on H-ZSM-5 in case of our catalyst may have decreased the strength of CHDEs adsorption and caused it to be reversible. Furthermore, HCl treatment of the Pt/H-ZSM-5 catalyst (Fig. 10c), seems to have increased the adsorption strength of CHDEs on Pt since their adsorption shifts more towards irreversibility such that their concentration in product becomes much lower.

It is evident that the largest maximum of CHDEs (Fig. 9) and the lowest yield of benzene (Fig. 12) are obtained using the H-ZSM-5 catalyst, whereas the lowest CHDEs and highest benzene yields are obtained using the Pt/H-ZSM-5(HCl) catalyst. The order of CHDEs maxima is as follows:



For benzene production, the yield is in the order:



This indicates that the catalyst possessing a higher activity for performing the hydrogenation reactions also possesses a higher activity for performing dehydrogenation reactions and vice versa. Both hydrogenation and dehydrogenation reactions are enhanced via improving the dispersion of platinum in the H-ZSM-5 zeolite support. This may lead us to conclude that both hydrogenation and dehydrogenation reactions are structure sensitive.

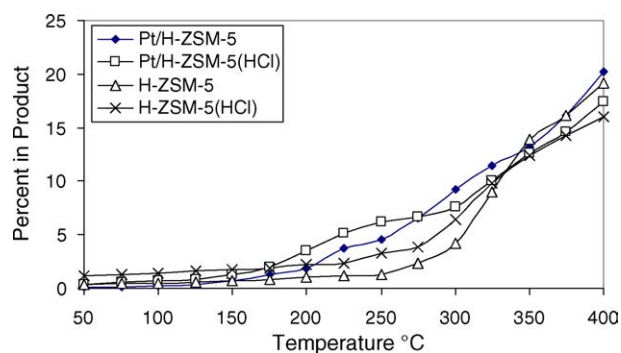
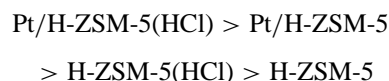


Fig. 11. Dehydrogenation reactions of CHE using HCl and/or Pt promoted H-ZSM-5 zeolite catalysts.

The overall dehydrogenation activity of each of the current catalysts has been calculated as: CHDEs + benzene + benzene ring in toluene and xylenes, and these values have been plotted as a function of reaction temperature for the current catalysts in Fig. 11. Evidently, the dehydrogenation activities at the low and high temperature ranges (50–200 °C and 325–400 °C, respectively) of all the current catalysts are not distinctly recognized; they are significantly overlapped. Nevertheless, during the intermediate region (200–325 °C) there appears some more distinct variation that can allow for a correlation of the dehydrogenation activities of the catalysts. Accordingly, these activities can be arranged in the order:



However, the Pt/H-ZSM-5 catalyst shows higher activity during the highest temperature region, which indicates that this catalyst does not suffer from diffusion limitation compared with the Pt/H-ZSM-5(HCl) catalyst which encounters diffusion restrictions, caused by chloro-aluminium debris. Anyhow (excluding this diffusion effect) it can be safely assumed that both hydrogenation and dehydrogenation activities have the same catalytic order (Fig. 12).

3.7. Production of alkylbenzenes

In addition to benzene production, other monocyclic alkylaromatics, namely; toluene and xylenes have been produced

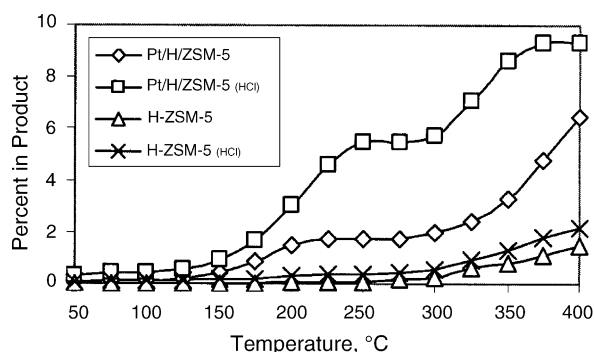


Fig. 12. Benzene in product using HCl and/or Pt promoted H-ZSM-5 catalysts.

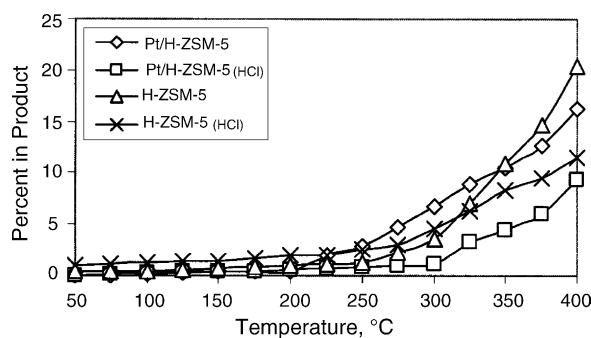


Fig. 13. Alkylation products of CHE using HCl and/or Pt promoted H-ZSM-5 zeolite catalysts.

during the process of CHE hydroconversion (Fig. 13). Gianetto et al. [47] have proposed schemes for the alkylation of CHE, CHDEs and benzene with cracked fragments, producing toluene and xylenes using acidic H-[Al]-ZSM-5 and bifunctional Ga/[Al]-ZSM-5 catalysts.

In the present work, at temperatures of 50–250 °C, alkylation to alkylaromatics is low on all current catalysts. From 250 to 400 °C, three out of the four current catalysts can be directly arranged in an activity order as follows:

Pt/H-ZSM-5 > H-ZSM-5(HCl) > Pt/H-ZSM-5(HCl)

Only, the mother H-ZSM-5 zeolite gives a curve exhibiting a low initial activity then becomes activated to surpass the activities of the others at 350 °C and above. This order does not conform to the order of acidity in Table 1, although alkylation is an acid catalysed reaction. Since both chlorinated catalysts give lower alkylating activities, it may be assumed that some amorphous extra-framework chloro-alumino-species has been deposited in the zeolitic channels and impeded the formation of the alkylated molecules. However, H-ZSM-5(HCl) is more active than Pt/H-ZSM-5(HCl), although Pt can act as an activator for the formation of the carbonium ion necessary for alkylation [48]. Pt in the zeolitic channels seems to have catalysed acceleration of forming the chloro-alumino-species which retarded alkylation. The highest activity encountered at high temperatures is realized by the mother H-ZSM-5 with its pores free from any amorphous debris or Pt.

The lower acidity strength of Pt/H-ZSM-5(HCl) than Pt/H-ZSM-5 can be attributed to masking a part of the strongest acid sites by the chloro-aluminium debris.

3.8. Hydrocracking reactions

During the hydroconversion of CHE, lower molecular weight hydrocarbons have been produced (Fig. 14). These hydrocarbons cannot be assumed to be products of CHE hydrocracking only, since a multitude of compounds are involved (Scheme 1). All of the current catalysts contain strong acid sites and hence possess cracking activities. However, two versions of these catalysts contain, in addition to the acid sites, a strong hydrogenating function (Pt sites) in addition to the acid sites. Such bifunctionality catalyses hydrocracking.

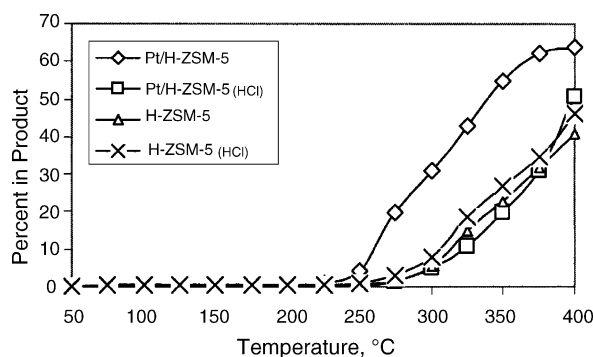


Fig. 14. Hydrocracking of CHE using HCl and/or Pt promoted H-ZSM-5 catalysts.

Fig. 14 shows that the hydrocracking reactions are very low at temperatures up to 250 °C using all current catalysts. Nevertheless, it is evident that three of the current catalysts; namely; H-ZSM-5, H-ZSM-5(HCl) and Pt/H-ZSM-5(HCl), acquire comparable hydrocracking activities (19.9–23.4% at 350 °C), whereas only the Pt/H-ZSM-5 catalyst is much more active for this reaction (54.7% at 350 °C). Comparing the hydrocracking activities of the H-ZSM-5 and H-ZSM-5(HCl) catalysts, it is evident that the chlorinated one is always slightly more active than the unchlorinated version, which can be attributed to the higher acid sites number and strength (Table 1). On the contrary, the chlorinated bifunctional Pt/H-ZSM-5(HCl) catalyst, which is expected to be the most active one, is found to be almost the least active. As mentioned above, the untreated Pt/H-ZSM-5 catalyst is the most active for this reaction, although it acquires the lowest acid sites number. However, this reaction requires acid sites with high strength; and this is realized using the Pt/H-ZSM-5 catalyst. The lower Pt dispersion and Pt surface area in the Pt/H-ZSM-5 catalyst than in Pt/H-ZSM-5(HCl) seem to have no role in greatly enhancing the hydrocracking reactions.

Hydrocracking is significantly affected by a physical factor, i.e. diffusion in the catalytic pores. Pore diffusion in the Pt/H-ZSM-5(HCl) catalyst seems to have been altered (restricted) by deposition of chloro-alumino species (debris) in the zeolitic channels formed via the HCl treatment. Compared to the little activation of H-ZSM-5 by HCl, it is recognized that Pt should have an active role in inhibiting the hydrocracking activity of Pt/H-ZSM-5 by HCl.

The two acid catalysed reactions, namely, alkylation (Fig. 13) and hydrocracking (Fig. 14) show similar influence on pore diffusivity limitation. Markedly, the masking of a part of the strongest acid sites in the bifunctional Pt/H-ZSM-5(HCl) catalyst by the debris has also contributed to inhibiting alkylation and hydrocracking. Even though, from a practical point of view, hydrocracking reactions are considered undesirable in the hydroisomerisation of light naphtha as well as in the catalytic reforming of heavy naphtha for octane improvement. Therefore, the post-chlorination of the Pt/H-ZSM-5 catalyst with 3.0% HCl looks to be a promising successful solution for inhibiting excessive hydrocracking to gaseous products, which are considered a loss of the liquid feeding naphthas.

4. Conclusion

In general, the activities of the current catalysts for CHE hydroconversion, hydrogenation and dehydrogenation are in the order: Pt/H-ZSM-5(HCl) > Pt/H-ZSM-5 > H-ZSM-5(HCl) > H-ZSM-5. The higher hydrogenation activity of the HCl doped Pt/H-ZSM-5(HCl) catalyst is attributed to increased Pt dispersion, whereas the higher activity of the H-ZSM-5(HCl) than H-ZSM-5 is attributed to the larger number of strong acid sites. At higher temperatures during CHE dehydrogenation, diffusion limitation seems to be encountered in the pores of the HCl treated Pt containing catalyst. This is attributed to deposition of small amounts of chloro-alumino species debris in the catalytic pores. The effect of this debris in restricting diffusion in the Pt/H-ZSM-5(HCl) catalyst is significantly manifested in the acid catalysed reactions, namely, alkylation and hydrocracking. The inhibition of hydrocracking seems economically of practical importance for improving the liquid yield in the naphtha hydroisomerisation and reforming processes. The step of CHE dehydrogenation to CHDEs can be considered rate determining in CHE dehydrogenation to benzene.

Our recently published work [50–52] shows that hydrogenation of CHE on mono- and bi-metallic catalysts supported on H-ZSM-5 is very active at low temperatures (50–150 °C), whereas on H-ZSM-5, whether promoted with HCl or not, hydrogenation of CHE is accomplished at significantly higher temperatures (250–350 °C).

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