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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.

Keywords: Cyclohexene; Hydrogenation; Isomerisation; Pt; Cyclohexadienes; Methylcyclopentenes; Benzene; Alkylbenzenes

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 Al_2O_3 [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-Al_2O_3 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-Al_2O_3(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/Al_2O_3 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-Al_2O_3 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/Al_2O_3 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/Al_2O_3 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 NH_4NO_3 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 $m^2\ g^{-1}$, a pore volume of 0.16 $cm^3\ g^{-1}$ 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 H_2PtCl_6 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 $cm^3\ min^{-1}$ 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 $8.33 \times 10^{-3}\ mol\ h^{-1}$; i.e. the H_2/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 CO_2 peak.