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Iridium/H-ZSM-5 zeolite catalyst promoted via hydrochlorination or hydrofluorination for the hydroconversion of cyclohexene

Ahmed K. Aboul-Gheit *, Noha A.K. Aboul-Gheit

Egyptian Petroleum Research Institute, Process Development Division, Nasr City, P.O. Box 9540, Cairo 11787, Egypt

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Abstract

The hydroconversion of cyclohexene (CHE) was carried out in a flow reactor at atmospheric pressure and temperatures of 50–400 °C using: Ir/H-ZSM-5, Ir/H-ZSM-5(HCl), and Ir/H-ZSM-5(HF) catalysts. The acid site strength distribution, Ir dispersion, XRD, SEM photography for these catalysts were evaluated. The hydroconversion reaction steps of CHE were found to proceed as follows: CHE → cyclohexane; CHE → methylcyclopentenes (MCPEs) → methylcyclopentane (MCPA); CHE → cyclohexadienes (CHDEs) → benzene; benzene → alkylbenzenes; CHE and others → hydrocracked products.

The doping of Ir/H-ZSM-5 catalyst with HCl enhanced its acid sites number and strength but reduced the Ir metal dispersion, whereas doping with HF enhanced acid sites number and strength as well as Ir metal dispersion. The hydrogenation step of CHE to CHA was significantly inhibited via HCl doping of Ir/H-ZSM-5 because of agglomeration of Ir crystallites, but significantly enhanced via HF doping due to improving Ir dispersion and increasing acid sites number and strength of the catalyst. Also, MCPEs hydrogenation and CHE dehydrogenation were highest on the untreated Ir/H-ZSM-5 catalyst because it doesn't suffer diffusion limitation caused by deposited halo-aluminium debris. CHE isomerisation does not critically depend on acid site parameters or on Ir dispersion in the catalysts. Hydrocracking reactions were more active on the HCl treated catalyst.

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

1. Introduction

Cyclohexene (CHE) hydroconversion on bifunctional catalysts passes through a number of reactions, each of which reflects a given behaviour of an active site type. Hence, CHE is frequently selected as a probe molecule for investigating catalyst preparation [1–4]. The experimental conditions; temperature, presence or absence of hydrogen, and the pressure of hydrogen show important changes in the catalytic behaviour. In 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 termed hydrogen transfer. When the reaction is carried out in presence of metal catalysts, 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, not strong enough to promote carbonium ion formation, and hence isomerisation and cracking reactions doesn't occur (monofunctional catalyst), whereas the H-forms of zeolites which possess strongly acidic Brönsted and Lewis sites can promote CHE isomerisation to a mixture of MCPEs and cracking to lower molecular weight hydrocarbons whereby the reaction scheme becomes more complicated (bifunctional catalyst). However, treatment of the cation-exchanged zeolites with aqueous HCl or HF acid leads to decationation and partial dealumination of the zeolite framework.

The results of isomerisation 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 both skeletal isomerisation and total conversion greatly increase [12].

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 hydroisomerisation, hydrocracking and dehydrocyclization of *n*-paraffins [14,16] using Pt/Al_2O_3 catalysts promoted with other metals (Rh, Ir, Re or U) as

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* Corresponding author.
E-mail address: aboulgheit2000@hotmail.com (A.K. Aboul-Gheit).

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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 of them on γ-Al_2O_3 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 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 doped with 1.0 wt.% Cl was tested in *n*-hexane reactions at 180–330 °C [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 iridium-loaded H-ZSM-5 catalysts have been doped with 3.0 wt.% HCl or HF to visualize their effects on CHE hydroconversion in a flow reactor operated in a flow of hydrogen gas 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. Ir/H-ZSM-5 catalyst

A part of H-ZSM-5 zeolite prepared in Section 2.1.1 was impregnated with an aqueous solution of chloroiridic acid (H_2IrCl_6) containing the requisite quantity to obtain 0.35 wt.% Ir. The catalyst was dried and calcined as in Section 2.1.1 then reduced in the catalytic reactor for 8 h at 500 °C before carrying out the reaction.

2.1.3. Ir/H-ZSM-5(HCl) catalyst

A part of Ir/H-ZSM-5 zeolite, prepared in Section 2.1.2 was doped with a solution containing the requisite quantity to contain 3.0 wt.% HCl. The catalyst was dried, calcined then reduced as above.

2.1.4. Ir/H-ZSM-5(HF) catalyst

A part of Ir/H-ZSM-5 zeolite prepared in Section 2.1.2 was doped with HF solution sufficient to contain 3.0 wt.% HF, dried, calcined then reduced as above.

All catalysts prepared in Sections 2.1.2–2.1.4 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 in the diffraction peak at 2θ of 10.88369° in the XRD diffraction patterns of both Ir/H-ZSM-5(HCl) and Ir/H-ZSM-5(HF) catalysts indicated slight bulk dealumination of the H-ZSM-5 zeolite.

2.2. Hydroconversion reactor system and reaction product analysis

The reactor is a silica-glass 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 a H_2 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 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 20M bonded in fused silica to be analysed using 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 current catalysts for CHE hydroconversion for time-on-stream of 180 min at 400 °C didn't show any decrease of the activities of the catalysts. Moreover, examination of these catalysts for carbon deposition using temperature programmed oxidation (TPO) in a differential scanning calorimeter (DSC) didn't show the CO_2 peak.

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 $cm^3\,min^{-1}$. 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 $cm^3\,min^{-1}$. The heating rate was 10 K min^{-1} and the full-scale range was 25 mW.