

# 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<sup>-</sup> 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

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 Al<sub>2</sub>O<sub>3</sub> [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<sup>-</sup> ions has been studied by Ozimek et al. [10,11]. Introducing Cl<sup>-</sup> 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/Al<sub>2</sub>O<sub>3</sub> catalysts promoted with other metals (Rh, Ir, Re or U) and Cl<sup>-</sup> or F<sup>-</sup>. 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 Kluskdahl [17], monometallic Re catalysts have not received

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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 Kluksdahl [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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was carried out at temperatures of 50–250 °C [9]. The effect of doping with 3.0 wt% of Cl<sup>-</sup> or F<sup>-</sup> 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 NH<sub>4</sub>NO<sub>3</sub> 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 m<sup>2</sup>/g, and pore volume of 0.16 cm<sup>3</sup>/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 diffraction (XRD) analysis. The main diffraction peak in all forms appeared at  $2\theta$  of 23.0°. However, a very slight increase in the diffraction peak at  $2\theta$  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  $\pm 1$  °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 H<sub>2</sub> flow passed into a closed jar thermostated at a fixed temperature of 28 °C whereby the quantity of cyclohexene fed to the catalyst was  $8.33 \times 10^{-3}$  mol/h, i.e., the H<sub>2</sub>/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 CO<sub>2</sub> peak.

### 1.3 Catalyst characterization

The temperature-programmed desorption (TPD) of pre-adsorbed 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 NH<sub>3</sub> 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 ex-

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