



Modifications of an HY zeolite for *n*-octane hydroconversion

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ABSTRACT

Solids based on HY zeolite were modified by either dealuminization (D) followed by chemical vapour deposition of silicon (CVD). Additionally, impregnation of Pt or Ni was performed over selected D and CVD solids. Samples were characterized by XRD, ²⁷Al and ²⁹Si NMR, acidity measurements, N₂ adsorption/desorption isotherms, Raman analysis and evaluated in *n*-octane hydroconversion at *P* = 1 atm and *T* = 300 °C. In comparison with the CVD and pure D series of solids, Pt impregnation on dealuminated HY resulted in a high level of isomerization products. Although the conversion upon using Ni-containing dealuminated HY was elevated, cracking products were predominant over this solid. The trends in the activity can be explained by the accessibility of acidic sites and their acidity. The catalytic activity follows the order PtCVD1 > NiD > PtD ~ D > CVD1. The combined effect of moderate acidity and Pt dispersion resulted in better catalytic performance for the PtCVD1 catalyst, which was active in the hydroisomerization reaction (conversion of 30%) with almost no coking on the sample, whereas cracking products were predominant over other solids. The characterization of spent catalysts showed no loss in activity, with low coke deposition on solid surface over the CVD1 sample in comparison with the D series of solids. Furthermore, mechanistic insights demonstrated that on PtCVD1, the adsorbed carbon species were formed via the cracking and oligomerization of *n*-octane precursors.

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1. Introduction

Hydrocracking and hydroisomerization of *n*-paraffins are important refinery processes used to produce highly valuable chemicals, such as high-octane reformulated gasoline, diesel and lubricating oil [1–5].

Hydroconversion reactions are efficiently carried out over bifunctional catalysts, consisting of a metal, which is responsible for hydrogenation–dehydrogenation reactions, and an acidic functionality, which is responsible for C–C and C–H bond activation [2,5]. Therefore, in order to promote the hydroisomerization reaction, different oxides, such as alumina, zirconia, and sulfides were applied to the reaction. Also, the zeolites (e.g., MOR, BEA, ZSM-5, MAZ, OFF, USY, ZSM-22, MCM-22), and zeolite-like solid acids (e.g., SAPO-11, AIPO-5, SAPO-41) have been used as acidic components together with a metal (i.e., Pt, Ni, Pd, Co, Mo, Ir, Ru, Rh, Re) [1–5].

Over zeolites, both process proceed through consecutive branching reactions (i.e., isomerization of *n*-paraffins), while

cracking reactions occur in parallel with isomerization [6,7]. However, recent studies [8] reported the benefits of using metallic platinum or palladium in zeolites, which is mainly due to the high stability and increased resistance of deactivation by coke upon using metal-containing zeolites. Additionally, Ni containing ZSM-5, BEA, and MOR zeolites were evaluated in the hydroconversion of *n*-octane, and their activities were interpreted on the basis of the accessibility of acidic sites [9]. According to these results, a BEA zeolite possessing Brønsted acidic sites of lower acid strengths than their MOR and ZSM-5 analogues led to a decrease in the cracking rate. Also, when comparing zeolites with large pores, like ZSM-12, BEA, MOR, USY, to those with small pore (e.g., L-zeolite), the former have been in focus due to their high activity. Other molecular sieves like Omega, VPI-5, UTD-I, SBA-15, Al-MCM-41 and MCM-48 have been investigated with respect to the isomerization of *n*-paraffins and have considerably good catalytic properties; however, none of them have managed to balance activity and hydrocracking product selectivity as well as USY zeolites [5].

Among the zeolites, USY has been tested successfully. USY consists of a highly hydrothermal steam Faujasite (FAU) type Y dealuminated zeolite having a secondary porosity obtained during the partial destruction of the zeolite, which results in the formation of mesopores. The so-called ultra stable FAU type Y zeolite (e.g., USY) is responsible for the facilitation of the diffusion of larger molecules

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into zeolite channels, which is a pre-requisite of the hydroconversion application [5,6]. Although the role played by the acidic component of USY is fully described [3,5], some aspects related to acidic site roles in the *n*-octane hydroconversion must be clarified. Indeed, besides the extensive cracking of *n*-octane combined with low isomerization selectivities, the degree of coking of USY in *n*-octane hydroconversion should be minimized to improve the selectivity of multibranched species.

The aim of this work was to investigate the effect of acidic sites and pore structure on product selectivity and coke resistance of zeolite hydroconversion reactions (e.g., hydroisomerization and cracking). For this purpose, we aimed to gain insight into the characterization of acidic zeolites to identify the effects of acidity, structure and porosity on reaction pathways. The modifications of acidic sites of the FAU type Y zeolite were performed by dealumination (D) or chemical vapour deposition (CVD) (i.e., silanation). Platinum or nickel incorporation on D solid was lead to achieve superior activity and shape selectivity with bi-functional catalysts and to avoid coking of the FAU type Y zeolite.

Chemical vapour deposition (CVD) is efficiently used for the deposition of silicon oxide on porous substrates to modify both their porous structure and permeation properties [10]. In the case of silicon oxide deposition, the silica layer constitutes the final product of either thermal decomposition (pyrolysis) of the vapours of a silica precursor, such as tetraethoxysilane, or of oxidation reactions, which involve a silica source and an oxidizing reactant. This technique might allow the acidic sites of USY to be tuned. Also, metal impregnation on USY may provide a better dispersion of metals on the USY surface or inside the mesopores [11]; therefore, the manipulation of the physicochemical properties of D and CVD series of solids may be possible. This strongly suggests that the influence of the preparation method must be discussed in detail to explain which type of acidic sites or metal species act in *n*-octane hydroconversion. Mechanistic considerations were used to explain the catalytic performance of both series of solids.

To the best of our knowledge, this is the first time that a modified series of solids has been compared in the hydroconversion of *n*-octane under the conditions studied.

2. Experimental

2.1. Modifications of the solids

The Na-form of Faujasite type Y zeolite (Si/Al ratio of 5.6) was supplied by Union Carbide. The sodium Faujasite type Y was converted into the acidic form by treatment with a $1.0 \text{ mol L}^{-1} \text{ NH}_4\text{Cl}$ (30 mL g^{-1}) under agitation at 80°C for 12 h. The solid was then dried at 50°C and calcined at 500°C under air flow and the protonic non-dealuminated zeolite was designed as HY.

In order to develop an improved catalyst to *n*-octane hydroconversion reactions, the physicochemical properties of HY were modified by two methods: dealumination (D), and chemical vapour deposition silicon (CVD). Either Pt or Ni impregnation was performed for some selected samples of D and CVD series of solids.

The dealumination process (D) was performed on HY, as proposed by Almanza et al. [12,13]; the zeolite was heated in 12% H_2O -containing N_2 flow at 500°C for approximately 9 h. The solid was then refluxed in hydrochloric acid (3 mol L^{-1}) at 80°C for 1 h and subsequently washed, in order to remove chloride species. A final calcination was performed under air at 500°C for 2 h, leading to the ultra stable dealuminated FAU type Y sample, designated as D.

The surface modified, silylated molecular sieve was prepared by chemical vapour deposition of silica (CVD) on D, based on Chen et al. procedure [14] in order to control the acidity of this solid.

1.0 g of the sample was placed in a tubular cell and heat treated at 450°C under air flow (100 mL min^{-1}) for 5 h, then cooled to 150°C under nitrogen flow (100 mL min^{-1}). Silanation treatment of HY zeolite was carried out by passing a mixture of 4 wt.% TEOS (tetraethyl orthosilicate, Aldrich) in toluene through the catalyst at 150°C under nitrogen in a flow rate of 10 mL h^{-1} for 1 h of deposition time; subsequently the sample was calcined under air flow at 500°C , and denoted as CVD1.

The Pt or Ni containing catalysts were prepared by using the D solid and the impregnation method was conducted using an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in ethanol. The individual contents of the Pt and Ni were both close to 1 wt.%. A bimetallic sample, possessing near 0.5 wt.% of each metal (Ni ad Pt) was prepared according to Pinheiro et al. [15] and was used to investigate the catalytic performance in the hydroconversion of *n*-octane compared with the Ni and Pt containing catalysts.

The metal containing catalysts were dried at 100°C for 3 h and calcined at 600°C for 3 h under air flow. The calcined forms of the solids were designated as NiD, PtD and NiPtD. The CVD1 sample was also used as carrier for preparing a supported catalyst. The incipient impregnation wetness method with aqueous solutions of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Aldrich) was used to obtain near 1 wt.% of Pt on CVD1 support. Following the impregnation, the catalysts were dried at 100°C and calcined at 600°C for 3 h under air flow the solid was designated as PtCVD1.

2.2. Catalysts characterization

X-ray diffraction analyses of the catalysts were performed in the 2θ range of 10 – 80° in a Rigaku D-Max 240 diffractometer, using $\text{Cu K}\alpha$ radiation at 30 V and 40 mA.

The textural properties were examined from N_2 adsorption isotherms in a ASAP2000 Micromeritics equipment. Prior to analysis, all samples were degassed for 4 h at 150°C . The experiment was performed by nitrogen adsorption at -196°C . The surface area (BET method), were taken from the isotherms in the P/P_0 relative pressure range of 0.1–0.3.

The Si/Al ratio was measured in a Varian ICP-OES instrument. Previously, the samples were treated in a sand bath at 200°C with hydrofluoric acid and the subsequent dissolution with a 1 wt.% nitric acid solution.

The coke content of the solids was evaluated by means of Thermogravimetric analysis (TG). 50 mg of each solid was flushed with He (20 mL min^{-1}) from room temperature to 150°C in a Netsch equipment. The spent samples were burnt in order to determinate the carbon content, by using a flow of air from room temperature to 1000°C , with a heating rate of 5°C min^{-1} .

Pyridine adsorption–desorption measurements were monitored by IR. Self-supported wafers of 20 mg and 18 mm diameter were evacuated in situ in an infrared glass vacuum cell jointed with calcium fluoride windows. The cell was then connected to a vacuum system, and the samples were degassed under 10^{-5} Torr at 450°C for 4 h. IR spectra were recorded before as well as after pyridine adsorption at room temperature. Pyridine (Py) was then desorbed at increasing temperature (150, 250, and 350°C) in a dynamic vacuum, and recorded on a Hitachi spectrometer.

NMR experiments were carried out on a Bruker DSX 400 spectrometer. Samples were spun at 10 kHz in zirconia rotors and ^{27}Al chemical shifts were referenced to $\text{Al}(\text{H}_2\text{O})_6^{3+}$. Also, ^{29}Si and ^{27}Al NMR spectra were obtained on the equipment using a spinning frequency of 10 kHz.

Scanning electron microscopy (SEM) measurements were conducted on a JEOL JEM-2010 electron microscope, using an acceleration voltage of 200 kV for selected spent catalysts.

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