



Acid properties of the hybrid catalyst CuO–ZnO or CuO–ZnO–Al₂O₃/H-ferrierite: An infrared study

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ABSTRACT

The acid properties of hybrid catalysts based on CuO–ZnO or CuO–ZnO–Al₂O₃ supported on the H-ferrierite zeolite were studied by NH₃-TPD and FTIR using two molecular probes, pyridine and *d*₃-acetonitrile. The samples were prepared using two different methods. The acid strength of these hybrid catalysts was considerably reduced by decreasing the amount of zeolite, and by the partial blockade of the acid sites by the CuO–ZnO or CuO–ZnO–Al₂O₃ component. However, strong acid sites still remained in the catalyst prepared by coprecipitation–sedimentation. Highly dispersed phases of Cu, Zn, and Al oxides promoted a minor blockage of the zeolite acid sites. Pyridine has been shown to be a suitable molecular probe to identify the Bronsted and Lewis acid sites in the hybrid catalysts. More Lewis acid sites were formed, and a high reduction in Bronsted acid sites was observed in all samples compared to H-ferrierite zeolite. Infrared spectra of adsorbed *d*₃-acetonitrile for the hybrid catalysts varied according to the method used for preparation. Interaction between Si–OH and *d*₃-acetonitrile was observed only for the samples prepared by coprecipitation–impregnation. With acetonitrile, strong Lewis acid sites were observed in all samples, and band intensity was proportional to the amount of zeolite. Bronsted acid sites were only observed in samples prepared by coprecipitation–sedimentation.

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1. Introduction

Hybrid catalysts have been used in a wide range of chemical processes [1–5]. Constituted by the mixture of two or more components, they may catalyze more than one reaction. Each component presents an active site for one specific reaction. It is important that contact between both components does not cause the total blockage of each component's active site.

The synthesis of high quality fuel from methanol has recently drawn attention from fuel industries. Commercially, methanol is made from the synthesis of CO/H₂ gas, obtained from the steam reforming of natural gas or the gasification of coal. The technology of methanol conversion to hydrocarbons provides an indirect means to convert natural gas into fuels. The Cu–ZnO/SiO₂ system has been widely used in the production of methanol from gas synthesis, where the active copper site shows improved dispersion when supported [6]. Porous zeolite acid catalysts have presented interesting results in the hydrocarbon (HC) synthesis from methanol (HZSM-5, Mobil Oil Company) [1]. Hybrid catalysts formed by a methanol synthesis catalyst and a zeolite have been

used in the production of light-fraction hydrocarbons C₃ and C₄ (LPG–liquefied petroleum gas) from synthesis gas [1].

The transformation of methanol into hydrocarbons is carried out over the acid sites of the zeolite, mainly the strong acid sites. However, the acid properties of the zeolite are affected by the oxide mixture (CuO–ZnO) [1,7]. Contact between these components depends mainly on the preparation method. To study the influence of the methanol synthesis catalyst on the zeolite acidity, infrared measurements using different molecular probes have been performed [8–12] in addition to ammonia temperature-programmed desorption. The nature and concentration of acid sites at hybrid catalysts are extremely important. For this purpose, characteristic vibrations of OH groups and adsorption of molecular probes with different basicity such as pyridine, ammonium, and *d*₃-acetonitrile are used. Among these molecules, the strong base pyridine is able to interact with the acid sites and to distinguish the adsorption between the Bronsted and Lewis acid sites, being frequently applied. On the other hand, the H-ferrierite zeolite, formed by a channel structure with 8- and 10-membered rings, presents a geometric limitation to the use of large molecular probes [11]. Given the higher limitation for molecular probe penetration into zeolite channels in the case of hybrid catalysts due to the partial blockage of the acid sites by the methanol synthesis catalyst, the use of a small molecule probe becomes necessary. For this purpose, *d*₃-acetonitrile (CD₃–CN) constitutes an alternative for the determi-

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nation of acid sites in hybrid catalysts. In the case of the H-ferrierite zeolite, the C=N group from d_3 -acetonitrile interacts with the Bronsted and Lewis acid sites [12,13].

This work studies the nature of acid sites in hybrid catalysts based on Cu–ZnO and Cu–ZnO–Al₂O₃ supported on the H-ferrierite zeolite. Infrared spectroscopy of adsorbed pyridine and d_3 -acetonitrile were used, as well as the NH₃-TPD technique to measure and identify acid strength. The catalysts were prepared through coprecipitation–impregnation and coprecipitation–sedimentation methods to evaluate the influence of each method on the hybrid catalyst acidity.

2. Experimental

2.1. Hybrid catalyst preparation

Samples were prepared using the coprecipitation–impregnation and coprecipitation–sedimentation methods. Catalysts were based on CuO/ZnO (Cu/Zn=2 molar ratio) or CuO/ZnO/Al₂O₃ (Cu/Zn/Al=55/30/15 molar ratio), both supported on the H-ferrierite zeolite. The expected ratios between the methanol synthesis catalyst (MSC) and the zeolite (HF) were 0.8 and 1.2 for the samples prepared by coprecipitation–sedimentation, and 0.64 and 1.2 for the samples prepared by coprecipitation–impregnation. These preparation methods were based on the technique described by Huang et al. [3]. Coprecipitation–impregnation consisted of the mixture of two solutions, Cu and Zn nitrates (0.66 mol/L), and sodium carbonate (0.8 mol/L) dropped simultaneously over an H-ferrierite zeolite suspension maintained at 80 °C and pH 7, under vigorous stirring. The formed precipitates were aged for 1 h at 80 °C. Then, the sample was washed with de-ionized warm water and dried for 12 h at 90 °C. For the coprecipitation–sedimentation method, an aqueous solution of Cu and Zn nitrate and an aqueous solution of Na₂CO₃ were simultaneously added to a beaker containing de-ionized water at 80 °C and pH 7. The precipitates were aged for 1 h and washed with warm water. The suspension was then added to an H-ferrierite zeolite suspension at room temperature and stirred for 1 h. The final suspension was centrifuged to separate the solid, which was dried at 90 °C for 12 h. The samples were calcined with N₂ at 400 °C, for 4 h. The nitrate salt solution and carbonate concentrations (1 mol/L each), and also the aging time (2 h) for the samples based on Cu, Zn, and Al were established according to Fierro et al. [14]. The original NaK-ferrierite zeolite was changed repeatedly with an NH₄NO₃ solution (1.7 mol/L) at 90 °C to obtain the H-form.

The catalysts were codified as follows: the first letters correspond to metals used in the methanol synthesis catalyst (CZ, Cu and Zn; CZA, Cu, Zn and Al); the two last letters correspond to the preparation method (CI, coprecipitation–impregnation; CS, coprecipitation–sedimentation), and finally the letters A or B corresponds to the methanol synthesis catalyst/H-ferrierite zeolite ratio (MSC/HF).

2.2. Catalyst characterization

The chemical composition of the studied samples, as determined by AAS, is given in Table 1. Phase identification and purity were evaluated by recording X-ray diffractograms using Rigaku D/MAX-1400 diffractometer with Cu K radiation α , with a tension of 40 kV and a current of 30 mA, the angle 2θ being covered between 5° and 80°.

The temperature-programmed desorption of ammonia (NH₃-TPD) measurements were carried out in a conventional TPR/TPD apparatus equipped with a quadrupole mass spectrometer

(Baltzer). The NH₃/He mixture (3.84 wt% NH₃) was flowed for 1 h over 200 mg of catalyst, at 175 °C. After adsorption, the sample was purged with He for 1 h at 175 °C. NH₃-TPD data were collected from 175 °C to 1000 °C at a rate of 10 °C min⁻¹.

FTIR spectra were recorded using sample waffles of thickness ca. 10 mg cm⁻². The samples were calcined at 400 °C in N₂ atmosphere for 2 h, and then evacuated to a pressure of 10⁻⁶ Torr. Pyridine and d_3 -acetonitrile were obtained from Aldrich Chem. Co., and were degassed by freeze–pump–thaw cycles. Adsorption of pyridine on the evacuated samples was carried out at 150 °C for 1 h followed by evacuations at 25 °C, 150 °C, and 250 °C for 30 min. d_3 -Acetonitrile was adsorbed at 25 °C for 30 min, followed by evacuations at 25 °C, 150 °C, and 250 °C.

The FTIR analyses were recorded on a Nicolet Nexus-470 FTIR spectrometer with 4 cm⁻¹ resolution by collecting 120 scans for a single spectrum. Spectra were recorded at room temperature and the bands were deconvoluted using a procedure consisting of band position identification in a second spectrum derivative mode using the least square minimalization routine, approximating the bands using a Gaussian profile.

3. Results and discussion

3.1. Chemical composition and XRD

The ratios between metallic elements in the hybrid catalysts (Cu, Zn and Al) were very close to expected values. The MSC/HF ratio presented differences compared with expected values due to the precipitation conditions that do not allow all material to precipitate (Table 1). Catalysts based on Cu and Zn presented XRD peaks corresponding to the oxidized phases of these metals. These peaks were more intense in the samples with a higher MSC/HF ratio (Fig. 1A). Catalysts based on Cu, Zn and Al did not present peaks corresponding to these phases. In these cases oxidized phases highly dispersed with smaller particle sizes were formed. This effect was a consequence of the precursor hydroxycarbonated hydrotalcite formed in these samples. The hydrotalcite phase is favored when the Cu/Zn/Al atomic ratios are 55/30/15 (Fig. 1B). All hybrid catalysts also showed peaks corresponding to H-ferrierite zeolite.

3.2. Textural properties

Table 2 shows the textural property results for hybrid catalysts and the H-ferrierite zeolite. There was a reduction in the hybrid catalysts' textural properties compared to the pure zeolite. This is due to the zeolite only being part of the hybrid catalyst, while the textural properties represent a mixture of both components. As the MSC/HF ratio was reduced, an increase in the micropores area was observed due the higher zeolite amount. In the samples prepared by coprecipitation–impregnation, an increase in the external area was observed, with respect to zeolite and to others

Table 1
Chemical composition of hybrid catalysts

Catalysts	wt%			Ratio		
	Cu	Zn	Al	Cu/Zn	Cu/Zn/Al	MSC/H-ferrierite
CZCI-A	24	15	–	1.6	–	1.01
CZCI-B	20	11	–	1.8	–	0.59
CZACI-A	20	12	5.5	–	53/32/15	0.92
CZACI-B	16	7	5.2	–	57/25/18	0.64
CZCS-A	30	18	–	1.7	–	1.41
CZCS-B	22	12	–	1.8	–	0.87
CZACS-A	21	8.6	5.9	–	59/24/17	0.99
CZACS-B	15	7.4	3.9	–	57/28/15	0.58

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