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Synthesis, characterization and reactivity of high hydrothermally stable Cu-SAPO-34 materials prepared by "one-pot" processes

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ABSTRACT

A Cu-SAPO-34 material with very high activity for selective catalytic reduction (SCR) of NOx and hydrothermal stability has been synthesized following a sequential rationalized design. By using specific combinations of organic structure directing agents (OSDAs) and gel compositions in a "one-pot" method, it was possible to control Cu occupancy, framework Si distribution, and to maximize the yield of solids. The amount of Cu^{2+} is maximized and remains stable even after steaming at 750 °C for 13 h.

1. Introduction

The design of an attractive heterogeneous catalyst for a relevant chemical process involves the synthesis of materials with high activity, selectivity, and stability. Moreover, if the catalyst is mean to be used industrially, the synthesis procedure should be economically competitive. In many cases, the combination of innovative work together with accumulated knowledge allows to achieve new synthesis that not only improves the physico-chemical properties of the catalysts but also can meet the economical targets.

In the last years, the synthesis of small pore zeolites with large cavities containing extra-framework cationic metals, such as Cu^{2+}, has received much attention, thanks to their excellent activity and stability for the selective catalytic reduction (SCR) of NOx [1].

Traditionally, copper species are introduced in small pore zeolites by post-synthesis cationic exchange-impregnation methods [1,2]. However, the distribution of Cu within the zeolitic crystals following these procedures can be limited by diffusion of the Cu due to the presence of small pores (openings ~3.5 Å), being the metal preferentially located close to the external surface [3]. To avoid this, different "one-pot" synthesis methods introducing organo-copper complexes in the synthesis gel have been recently described [4]. These direct procedures permit better metal dispersion within zeolitic crystals, and also allow reducing the overall synthesis steps required to achieve the final Cu–zeolite catalyst [5]. Diverse Cu-complexes and synthesis conditions have been reported in the last years to direct the "one-pot" preparation of different small pore chabazite (CHA) polymorphs, as Cu-SSZ-13 [4a,6], and Cu-SAPO-34 [4b,7]. Despite the advances in the preparation, most of those materials present: low hydrothermal stability when treated under severe conditions (presence of steam at high temperatures) [4,7b], require the combination of expensive organic structure directing agents (OSDAs) [6], or their solid yields after crystallization are very low [7a].

In a previous report, we have described the direct preparation of Cu-SAPO-34 using a combination of diethylamine (DEA) and Cu-tetraethylenepentamine (Cu-TEPA) as organic structure directing agents (OSDAs) [4b]. In that study, we were able to synthesize Cu-SAPO-34 materials with high solid yields (>90 wt% of the initial oxide sources), and high catalytic activities for the SCR of NOx under severe reaction conditions when fresh and steamed samples at 600 °C were tested. However, when the samples were more intensively steamed at 750 °C for 13 h, a significant loss of catalytic activity was observed for Cu-SAPO-34 materials containing low Cu content, while the crystalline framework of Cu-SAPO-34 materials with medium-high Cu content collapsed [4b].

We present here an extensive and systematic study of the synthesis, characterization, and catalytic testing of Cu-SAPO-34 that

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has allowed unrevealing the key catalyst variables that control synthesis yield and hydrothermal stability. Then, by means of a one-pot synthesis procedure, it has been possible to prepare an efficient, very active and highly hydrothermally stable Cu-SAPO-34 catalyst. Deep characterization, including infrared spectroscopy (FTIR) using probe molecules, X-ray photoelectron spectroscopy (XPS), or temperature-programmed reduction (TPR) using H_2 as reducing gas, has shown the nature of the active sites and how they are preserved after hydrothermal treatment at 750 °C.

2. Experimental

2.1. Synthesis

2.1.1. Direct syntheses of Cu-SAPO-34 materials

In a general procedure for the Cu-SAPO-34 preparation, the Cu-complex was firstly prepared by mixing a 20 wt% of an aqueous solution of copper (II) sulfate (98 wt%, Alfa) with the tetraethylenepentamine (TEPA, 99 wt%, Aldrich). This mixture was stirred for 2 h until complete dissolution. Secondly, distilled water and phosphoric acid (85 wt%, Aldrich) were added and stirred for 5 min. Third, alumina (75 wt%, Condea) and silica (Ludox AS40 40 wt%, Aldrich) sources were introduced in the gel mixture. Finally, diethylamine (DEA, 99 wt%, Aldrich), tetraethylammonium bromide when required (TEABr, 99 wt% Sigma–Aldrich), and SAPO-34 seeds (5 wt% of expected final yield) were added into the gel, and the mixture was stirred for 30 min. The resulting gel was transferred to an autoclave with a Teflon liner, and heated at 150 °C under static conditions for five days. Table 1 summarizes the experimental conditions used for the synthesis of each sample. Crystalline products were filtered and washed with abundant water and dried at 100 °C overnight. The samples were calcined at 550 °C in air to properly remove the occluded organic species.

2.2. Characterization

Powder X-ray diffraction (PXRD) measurements were performed with a multisample Philips X'Pert diffractometer equipped with a graphite monochromator, operating at 45 kV and 40 mA, and using Cu Kα radiation (λ = 0.1542 nm).

The chemical analyses were carried out in a Varian 715-ES ICP-Optical Emission spectrometer, after solid dissolution in HNO_3/HCl/HF aqueous solution. The organic content of as-made materials was determined by elemental analysis performed with a SCHN FISONS elemental analyzer.

MAS NMR spectra were recorded at room temperature with a Bruker AV 400 spectrometer. ^{29}Si NMR spectra were recorded with a spinning rate of 5 kHz at 79.459 MHz with a 55° pulse length of 3.5 μs and repetition time of 180 s. ^{13}C MAS NMR cross-polarization (CP) spectrum was recorded at a sample spinning rate of 5 kHz. ^{29}Si, and ^{13}C chemical shifts were referenced to tetramethylsilane, and adamantane, respectively.

UV–Vis spectra were obtained with a Perkin–Elmer (Lambda 19) spectrometer equipped with an integrating sphere with $BaSO_4$ as reference.

Temperature-programmed reduction (TPR) experiments were performed in a Micromeritics Autochem 2910 equipment.

FTIR experiments were recorded with a Thermo "Nexus" spectrometer equipped with a DTGS detector. The infrared cell was designed to treat the samples in situ under vacuum or under flow conditions. For CO and NO adsorption experiments, the sample has been activated under oxygen flow at 350 °C for 2 h, followed by vacuum treatment (10^{-5} mbar) at 150 °C for 1 h. Vacuum treatment under this condition is not reductive according to literature data [8]. After activation, the samples have been cooled down under vacuum conditions to −175 °C. At this temperature, CO or NO has been adsorbed in the pressure ranged between 0.2 and 2 mbar for CO and 0.05 and 0.6 mbar for NO. Deconvolution of the IR spectra has been done using the ORIGIN software.

X-ray photoelectron spectra were collected using a SPECS spectrometer with a 150-MCD-9 detector and using a non-monochromatic Al Kα (1486.6 eV) X-Ray source. Spectra were recorded at −175 °C, using analyzer pass energy of 30 eV, an X-ray power of 50 W and under an operating pressure of 10^{-9} mbar. During data processing of the XPS spectra, binding energy (BE) values were referenced to P2p peak (135.5 eV). Spectra treatment has been performed using the CASA software.

2.3. Catalytic experiments

The activity of the samples for the selective catalytic reduction (SCR) of NOx using NH_3 as reductor was tested in a fixed bed, quartz tubular reactor of 1.2 cm of diameter and 20 cm length. The total gas flow was fixed at 300 ml/min, containing 500 ppm of NO, 530 ppm of NH_3, 7% of O_2, and 5% of H_2O. The catalyst (40 mg) was introduced in the reactor, heated up to 550 °C, and maintained at this temperature for one hour under nitrogen flow. Then, the desired reaction temperature was set (170–550 °C) and the reaction feed admitted. The NOx present in the outlet gases from the reactor were analyzed continuously by means of a chemiluminescence detector (Thermo 62C).

Table 1
Molar ratios used for the synthesis of each Cu-SAPO-34.

Sample[a,b]	P/Al	Si/Al	Si/(Al + P)	Cu-TEPA/(Al + P)[c]	DEA/(Al + P)[d]	TEA/(Al + P)[e]
SAPO34-8	0.8	0.36	0.2	0.1	0.4	–
SAPO34-7	0.8	0.36	0.2	0.05	0.45	–
Cu-1	0.9	0.19	0.1	0.05	0.45	–
Cu-2	0.9	0.19	0.1	0.025	0.475	–
Cu-3	0.8	0.2	0.11	0.05	0.45	–
Cu-4	0.8	0.2	0.11	0.025	0.475	–
Cu-5	0.75	0.25	0.143	0.05	0.45	–
Cu-6	0.75	0.25	0.143	0.025	0.475	–
Cu-7	0.7	0.3	0.176	0.05	0.45	–
Cu-8	0.7	0.3	0.176	0.025	0.475	–
Cu-9	0.7	0.3	0.176	0.05	0.15	0.3

[a] All materials were prepared with H_2O/(Al + P) = 10 and 5 wt% of SAPO-34 crystals as seeding.
[b] All materials were crystallized at 150 °C for 5 days.
[c] Cu-tetraethylenepentamine.
[d] Diethylamine.
[e] Tetraethylammonium.