Journal of Catalysis 319 (2014) 36–43

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Direct synthesis design of Cu-SAPO-18, a very efficient catalyst for the SCR of NOx

Raquel Martínez-Franco, Manuel Moliner *, Avelino Corma *

Instituto de Tecnología Química (UPV-CSIC), Universidad Politécnica de Valencia, Consejo Superior de Investigaciones Científicas, Valencia 46022, Spain

ARTICLE INFO

Article history:
Received 5 June 2014
Revised 1 August 2014
Accepted 9 August 2014
Available online 6 September 2014

Keywords:
One-pot synthesis
Silicoaluminophosphate
SAPO-18
Selective catalytic reduction (SCR)
Nitrogen oxides (NOx)

ABSTRACT

The combination of Cu(II) triethylenetetramine and N,N-dimethyl-3,5-dimethylpiperidinium as structure directing agents allowed the direct preparation of highly active and hydrothermally stable Cu-SAPO-18 for the selective catalytic reduction of NOx with NH_3. The approach allows performing a one-pot synthesis avoiding intermediate calcination and ion exchange, while achieving complete framework Si isolation. Combination of physicochemical characterization techniques show that copper exists as extra-framework Cu^{2+}, which have been identified as the specific active sites for the SCR of NOx. The selective presence of isolated Si species in the zeolitic framework introduces high hydrothermal stability.

1. Introduction

In the last decades, small pore zeolites containing large cavities in their structure have become important industrial catalysts for the methanol-to-olefins (MTO) process, and for the field of gas separation [1]. In addition, these materials have recently broadened their applicability as efficient catalysts to control the emission of harmful gases, particularly nitrogen oxides (NOx) mainly produced during the high temperature combustion in diesel engines [1,2]. Indeed, the selective catalytic reduction (SCR) of NOx by ammonia or urea has been reported as the most widely applied emission control [3], and copper-exchanged small pore CHA materials as one of the preferred catalysts (either as silicoaluminate, Cu-SSZ-13 [1,2,4], or as silicoaluminophosphate, Cu-SAPO-34) [2,5].

Small pore Cu-CHA shows higher catalytic activities and hydrothermal stabilities for the SCR of NOx than other previously studied zeolites with larger pores (as Cu-Beta or Cu-ZSM-5, among others) [6]. This is a very important point because the SCR of NOx reaction is performed in the presence of steam at high temperatures (above 400 °C) and, under these severe conditions, Cu-Beta or Cu-ZSM-5 zeolites suffer from permanent deactivation [6]. Specific stabilization issues by coordination of extra-framework Cu^{2+} cations to three oxygen atoms of the double 6-rings (D6R) units present in the CHA structure have been described as the main reason of the improved catalytic activity and hydrothermal stability of the Cu-CHA catalysts [7].

Besides Cu-exchanged CHA, other Cu-exchanged small pore silicoaluminates containing D6R in their structure have been reported as efficient catalyst for the SCR of NOx, as Cu-SSZ-16 [8] and Cu-SSZ-39 [9]. Particularly, Cu-SSZ-39, which presents the AEI structure, shows very high catalytic activity and hydrothermal stability for the SCR of NOx, even higher than commercial Cu-SSZ-13 catalyst [9]. Unfortunately, the range of preparation conditions of the silicoaluminate SSZ-39 is very limited, requiring very narrow Si/Al synthesis ratios ($\sim$30) and specific chemical sources, as for instance partially dealuminated USY and sodium silicate as Al and Si sources, respectively [10]. Moreover, the relatively low Si/Al ratios of the final SSZ-39 materials ($\sim$7–10) compared to the synthesis Si/Al ratios, indicate that the solid yields are low (<50 wt% of initial oxides) [9,10], and this fact precludes possible industrial applications.

The AEI structure has also been reported as silicoaluminophosphate form, SAPO-18 [11], which is mainly synthesized using N,N-diisopropylethylamine (DIPEA) as organic structure directing agent (OSDA) [11,12]. SAPO-18 has been thoroughly used as catalyst for the MTO reaction [13], but very few descriptions can be found in the literature for the SCR of NOx using Cu-exchanged SAPO-18 [14]. Indeed, these Cu-exchanged SAPO-18 materials show moderate SCR-DeNOx catalytic activities and low hydrothermal stabilities, probably as a result of the large presence of Si-rich domains as Si islands. In fact, the formation of these Si-rich

---

* Corresponding authors.
E-mail addresses: mmoliner@itq.upv.es (M. Moliner), acorma@itq.upv.es (A. Corma).

http://dx.doi.org/10.1016/j.jcat.2014.08.005
0021-9517/

domains take place by multiple substitutions of Al^{3+} and P^{5+} with Si^{4+} atoms in tetrahedral coordination, resulting in neutral silicon domains that very weakly stabilize the extra-framework cationic species [15,16]. In contrast, if a selective isomorphic substitution of P^{5+} with isolated Si^{4+} atoms in tetrahedral framework positions may take place, an improved stabilization of the extra-framework cationic species and, consequently, of the overall catalyst may occur by the selective introduction of negative charges in the zeolitic framework [11].

Very recently, different direct syntheses of Cu-containing small pore zeolites, especially CHA polymorphs, have been reported in the literature using inexpensive cationic organometallic complexes [5a,5b,16,17]. These "one-pot" syntheses procedures are very interesting because the multiple steps required in the conventional post-synthetic metal ion-exchange methodologies (zeolite synthesis, calcination, cationic exchange, and calcination) are avoided. The direct synthesis of metal-containing zeotypes not only allows optimizing the preparation of these materials in terms of reducing the number of synthesis steps, but also improving their physico-chemical properties [16]. For the particular case of Cu-SAPO-34, the hydrothermal stability of this catalyst has been considerably increased by properly modifying the synthesis conditions to favor the selective distribution of isolated Si species in the framework positions by direct synthesis methodologies [16].

Herein, we propose for the first time the direct synthesis of Cu-SAPO-18 to obtain a highly active and hydrothermally stable catalyst for the SCR of NOx. To do this, a rationalized use of cooperative OSDAs is proposed, consisting in the combination of an organometallic Cu-complex (Cu^{2+} with tetraethylenepentamine [TEPA] or triethylenetetramine [TETA]) with another organic molecule able to direct the crystallization toward the SAPO-18. The use of the N,N-dimethyl-3,5-dimethylpiperidinium (DMDMP) as co-template is shown for the first time to synthesize any aluminophosphate-related form of SAPO-18. Very interestingly, the direct synthesis of Cu-SAPO-18 materials by combining a Cu-polyamine complex and DMDMP as co-OSDA allows the crystallization of catalysts with high solid yields, isolated Si species in the zeolitic framework, controlled amount of extra-framework cationic species of copper in the final solids, and excellent catalytic activities and hydrothermal stabilities for the SCR of NOx.

2. Experimental

2.1. Synthesis

2.1.1. N,N-dimethyl-3,5-dimethylpiperidinium (DMDMP) synthesis

10 g of 3,5-dimethylpiperidine (Sigma–Aldrich, ⩾96 wt%) and 19.51 g of potassium bicarbonate ($KHCO_3$, Sigma–Aldrich; 99.7 wt%) were dissolved in 140 ml of methanol. Later, 54 ml of methyl iodide (CH_3I, Sigma–Aldrich, ⩾99 wt%) was added dropwise, and the mixture stirred at room temperature for 5 days. After this period, the mixture was filtered to remove most of the potassium bicarbonate, and the solution washed several times with chloroform. The combined organic extracts were dried over $MgSO_4$, filtered and finally, the quaternary ammonium salt (85% yield) was precipitated with diethyl ether. The iodide salt was converted to the hydroxide salt by treatment with a hydroxide anion-exchange resin (Dower SBR).

2.1.2. Direct synthesis of Cu-SAPO-18 materials

In a general procedure for the Cu-SAPO-18 preparation, the Cu-complex was first prepared by mixing a 20 wt% of an aqueous solution of copper (II) sulfate (98 wt%, Alfa) with the required amount of triethylenetetramine (TETA, 99 wt%, Aldrich) or tetraethylenepentamine (TEPA, 98 wt%, Aldrich). This mixture was stirred for 2 h until complete dissolution. Second, distilled water and phosphoric acid (85 wt%, Aldrich) were added to the above solution and stirred for 5 min. Third, the co-OSDA organic molecule, either N,N-diisopropylethylamine (DIPEA, 99 wt%, Aldrich) or N,N-dimethyl-3,5-dimethylpiperidinium (DMDMP) was introduced in the gel mixture. Finally, alumina (75 wt%, Condea) and silica (Ludox AS40 40 wt%, Aldrich) sources were added in 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 the desired temperature under dynamic conditions for the required time. 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.

2.1.3. Cu-exchanged SAPO-18

SAPO-18 was synthesized according to the procedure described in Ref. [11], using DIPEA as OSDA and the following molar gel composition: 1 Al_2O_3:0.85 P_2O_5:0.3 SiO_2:1.85 OSDA:18.5 H_2O. The crystalline sample was calcined at 550 °C in air to remove the occluded organic species. The calcined sample was washed with $NaNO_3$ (0.04 M), and afterward, cation exchanged overnight at room temperature with a $Cu(CH_3CO_2)_2$ solution (solid/liquid ratio of 100 g/l). The sample was filtered and washed with abundant distilled water and, finally, calcined at 550 °C for 2 h.

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 40 kV and 45 mA, and using Cu Kα radiation ($\lambda = 0.1542$ 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 on a SCHN FISONS element analyzer.

The morphology of the samples was studied by scanning electron microscopy (SEM) using a JEOL JSM-6300 microscope and by field emission scanning electron microscopy (FESEM) using a ZEISS Ultra-55 microscope.

The ^{29}Si MAS NMR spectra were recorded at room temperature with a Bruker AV 400 spectrometer MAS, with a spinning rate of 5 kHz at 79.459 MHz, a 55° pulse length of 3.5 μs and repetition time of 180 s. ^{29}Si chemical shift was referred to tetramethylsilane.

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

Temperature-programed reduction (TPR) experiments were carried out in a Micromeritics Autochem 2910 equipment.

2.3. Catalytic experiments

The catalytic activity of the samples for the selective catalytic reduction 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 of 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 1 h 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 was analyzed continuously by means of a chemiluminescence detector (Thermo 62C).