

Electronic Supplementary Information (ESI)

Efficient synthesis of the Cu-SSZ-39 catalyst for DeNO_x applications

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1.- OSDA and zeolite syntheses

Synthesis of OSDA N, N-dimethyl-3, 5-dimethylpiperidinium

10 g of 3,5-dimethylpiperidine (C_7H_{15} , Acros Organics, 96%, cis-trans mixture) was mixed with 140 mL of methanol (CH_3OH , Scharlab, 99.9%) and 19.51 g of potassium carbonate ($KHCO_3$, Sigma Aldrich, 99.7%). While this mixture was stirred, 54 g of methyl iodide (CH_3I , Sigma Aldrich, 99.9%) was added dropwise. The reaction was stirred for 7 days. After this time, MeOH was partially removed under vacuum, and the iodide salt was precipitated by addition of diethyl ether. For its use in the synthesis of zeolites, the final product was ion exchanged to the hydroxide form using a commercially available hydroxide ion exchange resin (Dowex SBR).

Synthesis of SSZ-39 zeolite using FAU zeolite as silicon and aluminum source and N, N-dimethyl-3,5-dimethylpiperidinium hydroxide as OSDA

The hydrothermal synthesis of AEI zeolite was carried out as follows. First the OSDA N,N-dimethyl-3,5-dimethylpiperidinium hydroxide was mixed with a 20%wt aqueous solution of sodium hydroxide (NaOH granulated, Scharlab). Then, the crystals of USY zeolite (CBV-720 with $SiO_2/Al_2O_3=21$) were introduced in this solution. The mixture was stirred until complete homogenization of the gel. The chemical composition of the synthesis gel was $SiO_2/0.045Al_2O_3/0.2NaOH/0.2OSDA/15H_2O$. The resultant gel was transferred into a stainless steel autoclave with a Teflon liner. The crystallization was then conducted at 135°C for 7 days under static conditions. The solid product was filtered, washed with water and dried at 100°C. Finally, the sample was calcined in air at 550°C for 4h.

Synthesis of SSZ-39 zeolite using FAU zeolite as silicon and aluminum source and tetraethylphosphonium hydroxide as OSDA

Phosphorous-containing SSZ-39 zeolite has been synthesized according to the method reported by Maruo et al.^[9] The chemical composition of the synthesis gel was $SiO_2/0.045Al_2O_3/0.1NaOH/0.2OSDA/5H_2O$, where OSDA corresponds to tetraethylphosphonium hydroxide. The crystallization was conducted at 150°C for 9 days under static conditions. The solid product was filtered, washed with water and dried at 100°C. Finally, the sample was calcined under a hydrogen atmosphere at

800°C for 4h to assure the complete decomposition of the phosphorous-containing species.

Post-synthetic Cu-exchange procedure on N-SSZ-39 and P-SSZ-39 materials

In order to perform the Cu ion exchange on the calcined SSZ-39 materials, the samples were exchanged with the required amount of a $\text{Cu}(\text{CH}_3\text{CO}_2)_2$ solution (solid/liquid ratio of 10g/L) at room temperature for 10 hours. Finally, the samples were filtered and washed with distilled water, and calcined in air at 550°C for 4 h.

“One-pot” synthesis procedure of Cu-SSZ-39

The one-pot synthesis of Cu-SSZ-39 was prepared using a mixture of Cu-TEPA complex and N,N-dimethyl-3,5-dimethylpiperidinium as cooperative OSDAs. First, the Cu-TEPA complex was in-situ prepared by mixing a 20wt% aqueous solution of copper (II) sulfate (CuSO_4 , Alfa Aesar, 98%) with the required amount of tetraethylenepentamine (TEPA, 98%, Sigma Aldrich). This mixture was stirred for 2 h. Then, aqueous solutions of the OSDA N-dimethyl-3,5-dimethylpiperidinium hydroxide and sodium hydroxide were added to the above Cu-TEPA solution. Finally, crystals of USY (CBV-720, $\text{SiO}_2/\text{Al}_2\text{O}_3=21$) were introduced as Si and Al sources to the mixture. The final composition of the synthesis gel was the following: SiO_2 / 0.045 Al_2O_3 / 0.05 Cu-TEPA / 0.4 OSDA / 0.2 NaOH / 25 H_2O . This gel was transferred to an autoclave with a Teflon liner and heated at 135°C under static conditions. The final solids were recovered and washed by filtration. The sample was calcined at 550°C in air for 4 hours to remove the organic species.

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 K α radiation ($\lambda = 0,1542$ nm).

The chemical analyses were carried out in a Varian 715-ES ICP-Optical Emission spectrometer, after solid dissolution in $\text{HNO}_3/\text{HCl}/\text{HF}$ aqueous solution. The organic content of the as-made materials was determined by elemental analysis performed with a SCHN FISIONS elemental analyzer.

The morphology of the samples was studied by field emission scanning electron microscopy (FESEM) using a ZEISS Ultra-55 microscope

^{27}Al MAS NMR spectra were recorded at room temperature with a Bruker AV 400 spectrometer at 104.2 MHz with a spinning rate of 10 kHz and 90° pulse length of 0.5 μs with a 1 s repetition time. ^{27}Al chemical shift was referred to $\text{Al}^{3+}(\text{H}_2\text{O})_6$.

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

3.- Catalytic experiments

The activity of the samples for the selective catalytic reduction (SCR) of NO_x 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 $^\circ\text{C}$ and maintained at this temperature for one hour under nitrogen flow. Then, the desired reaction temperature was set (170-550 $^\circ\text{C}$) and the reaction feed admitted. The NO_x present in the outlet gases from the reactor were analyzed continuously by means of a chemiluminiscence detector (Thermo 62C).

Figure S1: N₂ adsorption isotherm of the calcined N-SSZ-39 material

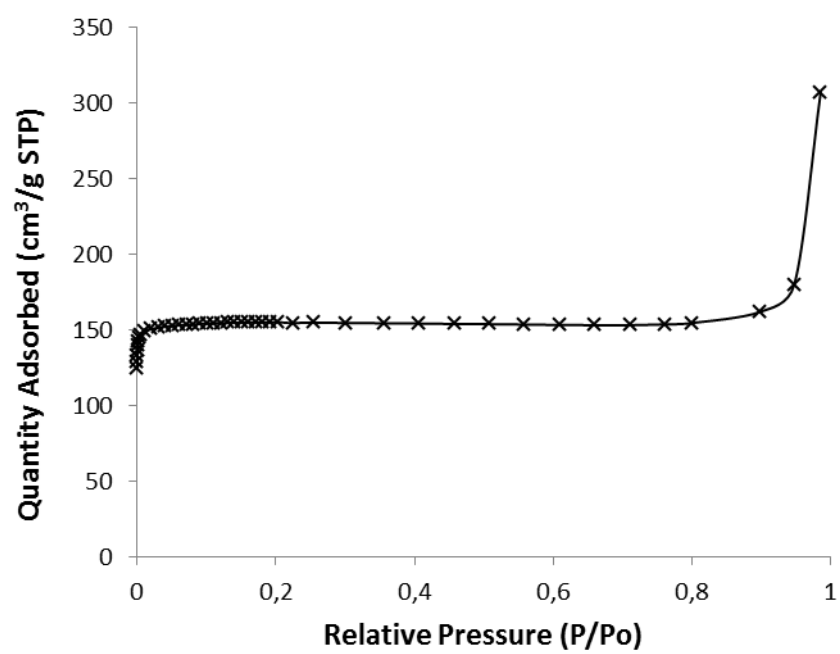


Figure S2: SEM images of a) N-SSZ-39 y b) P-SSZ-39

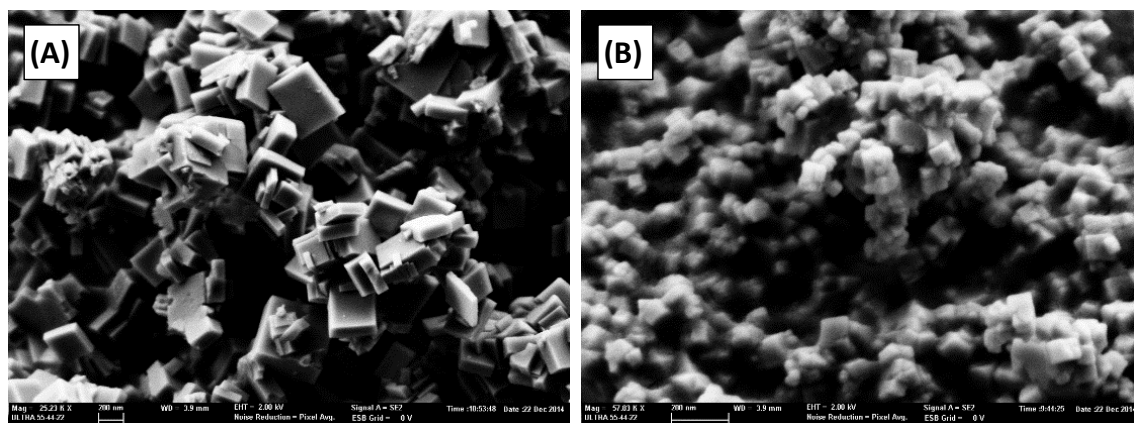


Figure S3: ^{27}Al MAS NMR spectra of SSZ-39 materials

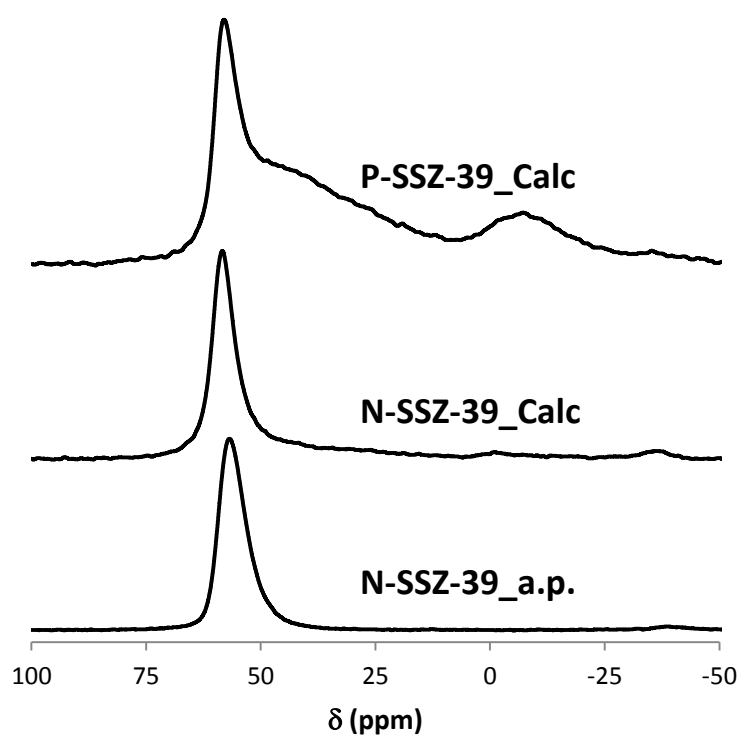


Figure S4: H₂-TPR profile of calcined Cu-containing SSZ-39 samples

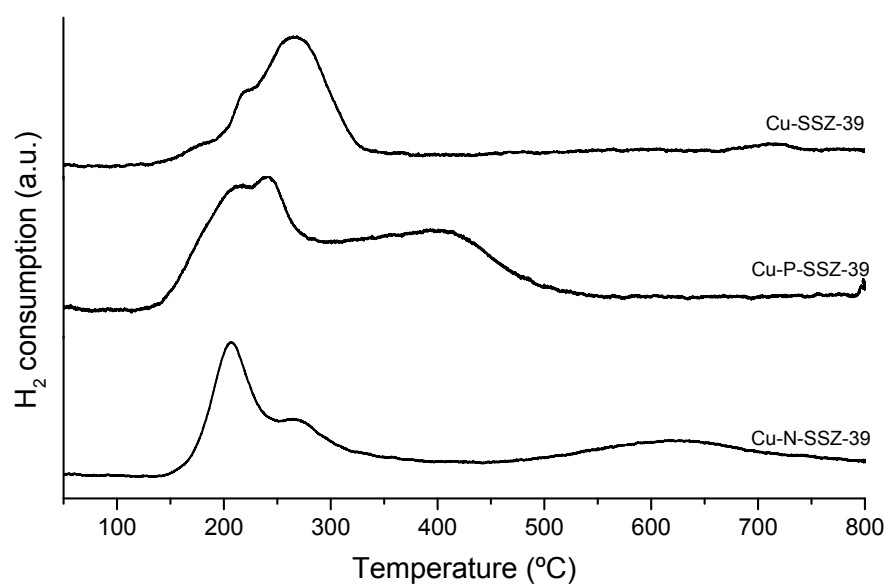


Figure S5: UV-Vis spectrum of the as-prepared Cu-SSZ-39 material

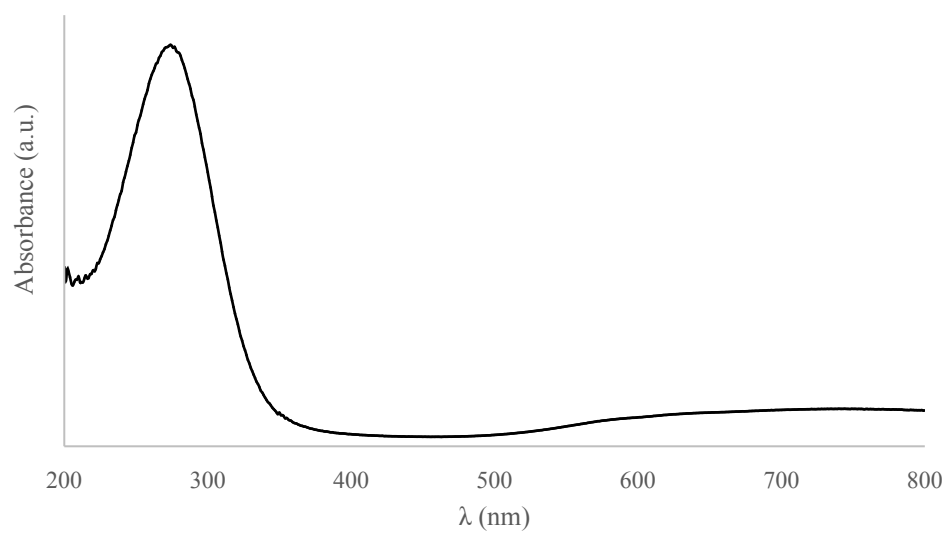


Table S1: ICP analyses of the zeolitic samples

<i>Sample</i>	<i>Si/Al</i>	<i>%wt Cu</i>
<i>N-SSZ-39</i>	8.2	---
<i>P-SSZ-39</i>	8.4	---
<i>Cu-N-SSZ-39</i>	8.1	4.7
<i>Cu-P-SSZ-39</i>	8.5	4.6
<i>Cu-SSZ-39</i>	9.9	3.3