Electronic Supplementary Information (ESI)

Cu-SSZ-39, an active and hydrothermally stable catalyst for the selective catalytic reduction of NOx

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1.- Experimental Methods

1.1.- Zeolite synthesis:

1.1.1.- Chabazite

The synthesis gel was prepared by hydrolizing 20.83 grams of tetraethylorthosilicate and 1.36 g of aluminium isopropoxide in 79.82 g of N,N,N-trimethyl-1-adamantamonium hydroxide 13.2 wt %. The mixture was evaporated at 298 K under gently stirring until complete evaporation of the alcohol formed during the hydrolysis of the reactants and the desired water content in the gel was reached. Finally, 2.08 g of HF (48 wt %) was added and the mixture was homogenized by mechanical stirring.

The molar ratio of CHA was:

$$SiO_2 : 0.033\ Al_2O_3 : 0.50\ SDAOH : 0.50\ HF : 3\ H_2O$$

where SDAOH is N,N,N-trimethyl-1-adamantamonium hydroxide.

The gel was autoclaved at 150ºC under tumbling. The final solids were recovered by filtration, washed with deionized water and dried at 373K

1.1.2.- SSZ-39 study

1.1.2.1.- SSZ-39-OSDA synthesis

The procedure for the OSDA manufacture is described next:

29.5 g of 3,5-dimethylpiperidine was mixed with 250 ml of methanol and 37.5 g of potassium carbonate. Then, 107.5 g of methyl iodide was added dropwise, keeping the reaction mixture under stirring for 7 days at room temperature. After reaction, the mixture was concentrated under vacuum and precipitated by addition of diethyl ether. The resultant solid was further extracted and washed with $CHCl_3$ to remove completely possible inorganic salts. The iodide salt was converted to the hydroxide salt by treatment with a hydroxide anion exchange resin.

1.1.2.2.- SSZ-39 experimental study

The procedure to perform the preparation of the samples described in the experimental design of Table S1 was:

The required amount of the OSDA salt in its hydroxide form and sodium hydroxide were mixture with water. Then, the Si source was introduced [LUDOX or sodium silicate, which has the composition: 25.63 wt% SiO_2, 6.05 wt % Na_2O], together with the Al source [USY_CBV500, Al_2O_3, $Al(OH)_3$]. The theoretical synthesis conditions for each sample are summarized in Table S1. Once each gel was prepared, it was introduced in an autoclave and heated at 135 °C for 7 days under static conditions.

1.2.- Cu-exchanged zeolites

The calcined zeolites were submitted to ionic exchange with an aqueous solution of $Cu(CH_3COO)_2$, containing the required Cu amount to afford the desired Cu exchanged (100% or 60%). The ionic exchange treatments were carried out at 25ºC overnight with a liquid to solid ratio of 100 ml Cu-solution per gram of zeolite. After the ionic exchange treatment, the solids were filtered and washed with abundant distilled water, and dried at 100ºC. Finally, the exchanged samples were calcined at 500ºC for 4 hours.

1.3.- Catalytic test

The activity of the samples for the selective catalytic reduction of NOx was tested in a fixed bed, quartz tubular reactor of 2.2 cm of diameter and 53 cm of length. In a typical experiment, the catalyst was prepared with a particle size of 0.25-0.42 mm. It was introduced in the reactor, heated up to 450ºC or 550ºC (depending on the reaction conditions, see Tables S2 and

S3 in ESI) and maintained at these temperatures for one hour under nitrogen flow. After that the desired reaction temperature was set and the reaction feed admitted. The SCR of NOx was studied with the different samples using NH_3 as reductor. The NOx present in the outlet gases from the reactor were analyzed continuously by means of a chemiluminiscence detector (Thermo 62C).

1.4 Hydrothermal steaming treatment

In order to test the hydrothermal stability of the zeolites, steaming treatments were done to the samples. They were exposed to water feed (2.2 mL/min) at 600 or 750ºC during 13 hours in a conventional oven (see Figure S2 in ESI).

2.- Characterization techniques

Synthesized samples were characterized by powder XRD using a multisample Philips X'Pert diffractometer equipped with a graphite monochromator, operating at 40 kV and 45 mA, and using CuKα radiation (λ=0.1542 nm).

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

The morphology of the samples was studied by scanning electron microscopy (SEM) using a JEOL JSM-6300 microscope.

3.- Tables

Table S1: Experimental design for SSZ-39 synthesis by using diverse sources of silicon and aluminium (OSDA/Si = 0.17, NaOH/Si = 0.02; T = 135ºC static conditions, t = 7 days).

Variable	Values	Number
Si sources	$NaSiO_3$ and LUDOX	2
Al sources	USY_CBV500, Al_2O_3, $Al(OH)_3$	3
Si/Al	15 and 30	2
H_2O/Si	20 and 40	2
	Total amount of experiments	***12***

Table S2: Chemical analysis of as-prepared samples

Sample	Si/Al (mol ratio)
SSZ-39 (Si/Al = 30)	9.1
SSZ-39 (Si/Al = 15)	7.4
CHA (Si/Al = 15)	12.7

Table S3: Mild reaction conditions.

Total gas flow (mL/min)	450
Catalyst load (g)	1
NO concentration (ppm)	500
NH_3 concentration (ppm)	530
O_2 concentration (%)	7
Testing temperatures (ºC)	250,350,450

Table S4: Severe reaction conditions

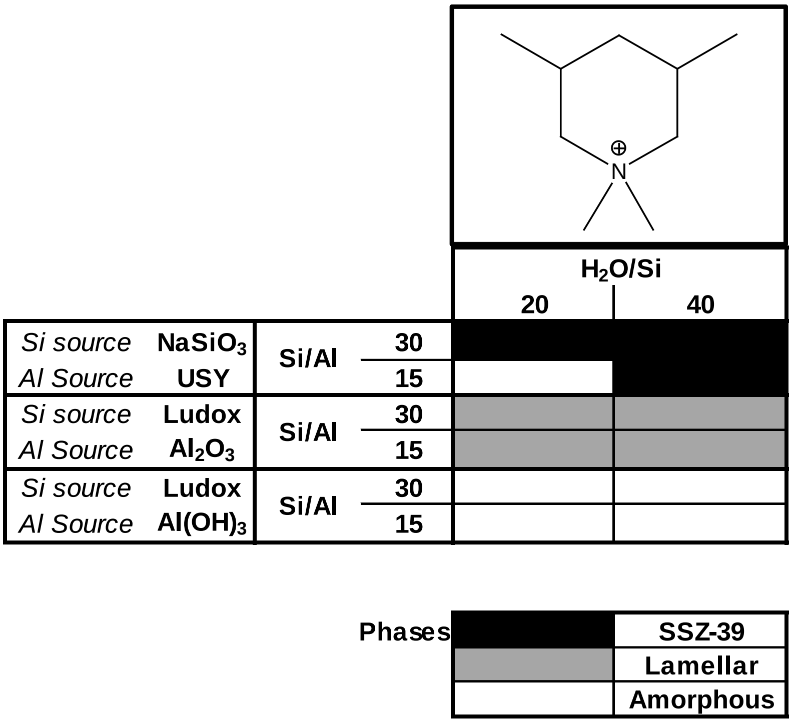
Total gas flow (mL/min)	300
Catalyst load (mg)	40
NO concentration (ppm)	500
NH_3 concentration (ppm)	530
O_2 concentration (%)	7
H_2O concentration (%)	5
Testing temperature interval (ºC)	170-550

Table S5: BET surface area, micropore area and micropore volume obtained from N_2 adsorption of calcined and steaming-treated CHA and SSZ-39 zeolites.

Sample	BET surface area (m^2/g)	Micropore area (m^2/g)	Volume micropore (cm^3/g)
SSZ-39_Calc	571	568	0.28
Cu-SSZ-39_600ºC	465	463	0.24
Cu-SSZ-39_750ºC	158	152	0.09
Cu-SSZ-39(60)_750ºC	530	524	0.26
CHA_calc	675	637	0.32
Cu-CHA_600ºC	633	585	0.29
Cu-CHA_750ºC	50	35	0.02

4.- Figures

Figure S1: Phase diagram obtained with the described experimental design (OSDA/Si = 0.17, NaOH/Si = 0.02, T = 135ºC, t = 7 days)



				H$_2$O/Si	
				20	40
Si source	**$NaSiO_3$**	**Si/Al**	**30**	■	■
Al Source	**USY**		**15**	□	■
Si source	**Ludox**	**Si/Al**	**30**	▨	▨
Al Source	**Al_2O_3**		**15**	▨	▨
Si source	**Ludox**	**Si/Al**	**30**	□	□
Al Source	**$Al(OH)_3$**		**15**	□	□

Phases		
	■	**SSZ-39**
	▨	**Lamellar**
	□	**Amorphous**

Figure S2: SEM images of (A) SSZ-39 (Si/Al = 15), (B) SSZ-39 (Si/Al = 30), and (C) CHA

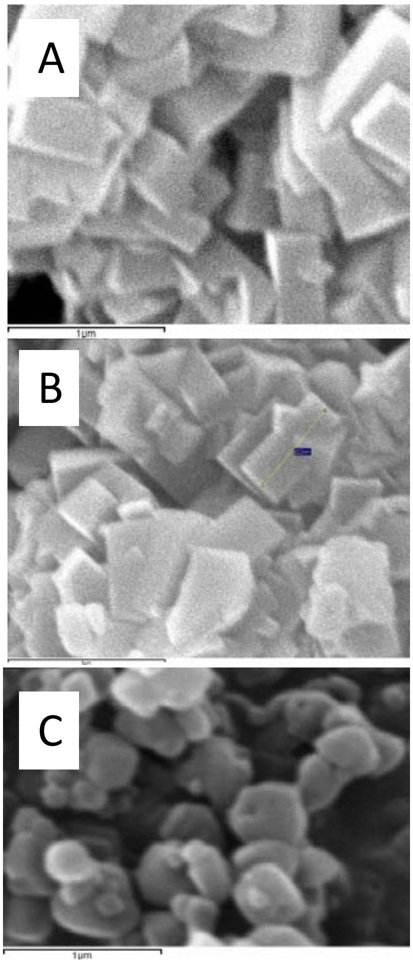


Figure S3: NH_3-SCR of NOx activity of Cu-SSZ-39 and Cu-CHA using laboratory conditions (see Table S3 in ESI).

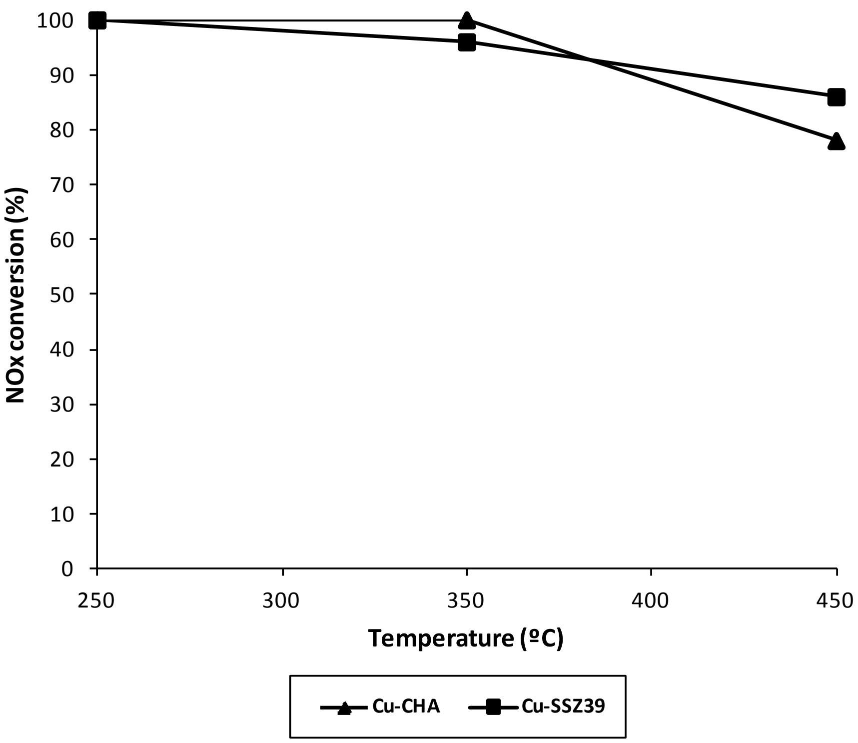


Figure S4: Temperature program used for the steaming treatment

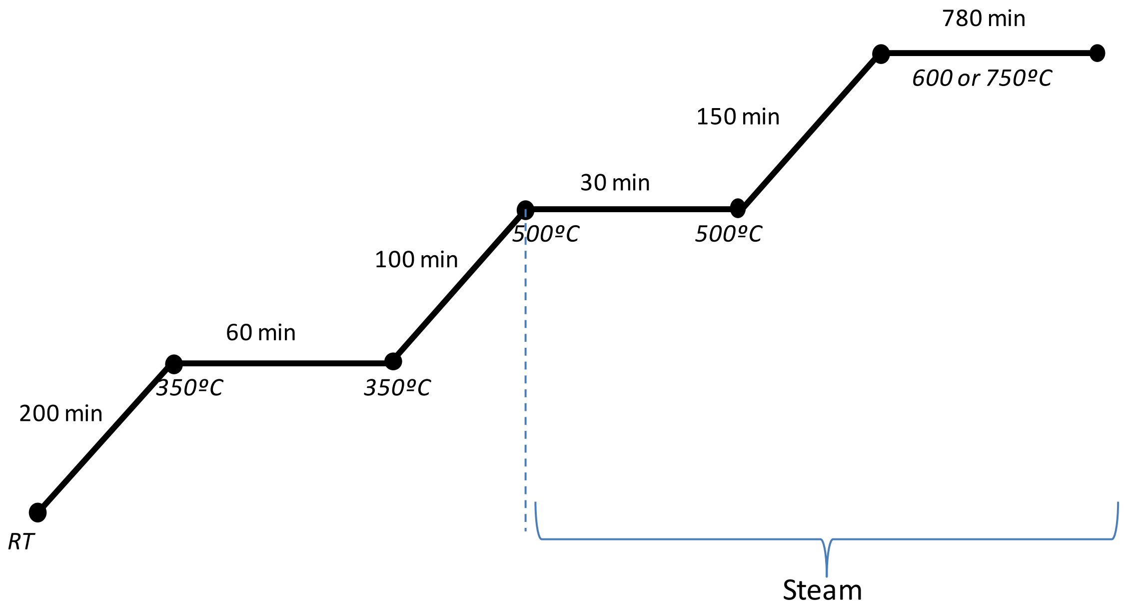


Figure S5: XRD patterns of Cu-CHA and Cu-SSZ39 zeolites after calcination and after steaming treatments (600ºC and 750ºC).