Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information (ESI)

High yield synthesis of high-silica chabazite by combining the role of zeolite precursors and tetraethylammonium. SCR of NOx.

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Experimental

1.- Synthesis

Synthesis of aluminosilicate zeolites using tetraethylammonium as OSDA and USY zeolite as silicon and aluminum source

For these type of synthesis, first the OSDA tetraethylammonium hydroxide (TEAOH, Sigma Aldrich, 35wt.%) was mixed with an aqueous solution of NaOH (Sigma Aldrich, 99%). Second, a commercial FAU zeolite (CBV-720, with measured molar ratios of $SiO_2/Al_2O_3=21$) was added to the mixture as aluminum and silica source. The stirring was continued until a homogenized gel was obtained. The gel was transferred to a stainless steel autoclave with a Teflon liner. The crystallization was conducted hydrothermally at 140 or 160ºC for 3 days under static conditions. The solid product was recovered by filtration, washed with water and dried at 100ºC.

For the particular case of the optimized CHA-1 material, the final gel composition for its preparation was SiO_2 / 0.047 Al_2O_3 / 0.2 TEAOH / 0.2 NaOH / 5 H_2O using CBV-720 as silicon and aluminum source. The crystallization was conducted hydrothermally at 433K for 3 days under static conditions. The solid product was recovered by filtration, washed with water and dried at 100ºC. Finally, the solid was calcined in air at 580ºC for 5 h.

It is important to note that CHA-1 material has been used as the **CHA** seeds for the experiments reported in Fig. S1 (†ESI).

Synthesis of aluminosilicate zeolites using tetraethylammonium as OSDA and different sources of Si and Al

For the purpose of checking the influence of the aluminum and silica source, Ludox (Sigma Aldrich, 40wt%), fumed silica (Aerosil) and MCM-41 were used as silica source and Al_2O_3 (75wt%) as aluminum source. In addition, a commercial Beta zeolite (CP811) with a Si/Al ratio of 12 has also been used as silicon and aluminum source.

First, Al_2O_3 was added to an aqueos solution containing NaOH (Sigma Aldrich, 99%) and TEAOH (Sigma Aldrich, 35wt%), and the mixture was stirred until a clear solution was obtained. Then, the appropriate silica source was added to the mixture. Once the different mixtures achieved the desired concentration, the gels were transferred to a stainless steel autoclave with a Teflon liner. The crystallization was then conducted hydrothermally at 140 or 160ºC for 3 days under static conditions. The solid product was recovered by filtration, washed with water and dried at 100ºC.

Post-synthetic Cu-exchange procedure on **CHA**

In order to perform the Cu ion exchange on the calcined CHA-1, the sample was exchanged with the required amount of a $Cu(CH_3CO_2)_2$ solution (solid/liquid ratio of 10g/L) at room temperature for 10 hours. Finally, the sample was filtered and washed with distilled water, and calcined at 550ºC for 4 h.

Direct synthesis of Cu-CHA-2 using TEA and Cu-TEPA as OSDAs

The procedure for the direct preparation of the Cu-CHA-2 zeolite was performed as follows: First, the Cu-complex was prepared by mixing a 20%wt aqueous solution of copper (II) sulfate (98%wt, Alfa) with the required amount of tetraethylenepentamine (TEPA, 99%wt, Aldrich). This mixture was stirred for 2 hours until complete dissolution. Second, the required amount of distilled water, NaOH (20%wt, Aldrich), and TEA hydroxide solution (35%wt) were added to the previous Cu-complex solution and stirred for 15 minutes. Third, commercial FAU zeolite (CBV-720, with measured molar ratios of SiO_2/Al_2O_3=21) was introduced in the gel mixture, and the resultant gel kept under stirring for 1 hour.

The final gel composition was SiO_2 / 0.047 Al_2O_3 / 0.05 Cu-TEPA / 0.4 TEAOH / 0.1 NaOH / 5 H_2O using CBV-720 as silicon and aluminum source. The gel was transferred to an autoclave with a Teflon liner, and heated at 433K under static conditions for 3 days. Crystalline products were filtered and washed with abundant water, and dried at 100ºC overnight. The sample was calcined at 550ºC in air to properly remove the occluded 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 usig 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 the as-made materials was determined by elemental analysis performed with a SCHN FISONS elemental analyzer. Thermogravimetrical analysis was performed using a Mettler Toledo thermo-balance.

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

MAS NMR spectra were recorded at room temperature with a Bruker AV 400 spectrometer. ^{27}Al MAS NMR spectra were recorded at 104.2 MHz with a spinning rate of 10 kHz and 9^{o} pulse length of 0.5 µs with a 1 s repetition time. ^{27}Al chemical shift was referred to $Al^{3+}(H2O)_6$.

Textural properties were determined by N_2 adsorption isotherms measured at 77 K with a Micromeritics ASAP 2020.

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 ºC and maintained at this temperature for one hour under nitrogen flow. Then, the desired reaction temperature was set (170-550ºC) and the reaction feed admitted. The NOx present in the outlet gases from the reactor were analyzed continuously by means of a chemiluminiscence detector (Thermo 62C).

Figure S1: Phase diagrams achieved using different Si sources (Ludox and Aerosil) and seeds of CHA (10%wt)

Si/Al = 12, NaOH/Si= 0.2, T = 160ºC, t = 3 days

		TEAOH/Si=0,2			TEAOH/Si=0,4		
		H_2O/Si			H_2O/Si		
		5	15	25	5	15	25
Si-source	LUDOX	▒	□	□	▒	▒	▨
	Aerosil	▒	□	□	▒	▒	▨

□	Non-tested
▒	BETA
▨	BETA+CHA

Figure S2: Phase diagrams achieved using different Si sources without seeding: (A) Ludox, (B) Aerosil, (C) MCM-41, (D) Beta zeolite

(A)

Si source: LUDOX Si/Al = 12, T = 140ºC, t = 3 days

		TEAOH/Si=0,2			TEAOH/Si=0,4		
		H_2O/Si			H_2O/Si		
		5	15	25	5	15	25
NaOH/Si	0,05	▨	▓		▒	▒	▧
	0,1	▒	▓	▓	▒	▒	▧
	0,2	▒	▦	▦	▒	▒	▨

	Amorphous
▒	BETA
▓	Amor+ZSM-12
░	ZSM-5
▨	BETA+ZSM-5
▦	ZSM-5+ZSM-12
▧	Beta+ZSM-12

Si source: LUDOX Si/Al = 12, T = 160ºC, t = 3 days

		TEAOH/Si=0,2			TEAOH/Si=0,4		
		H_2O/Si			H_2O/Si		
		5	15	25	5	15	25
NaOH/Si	0,05	░			▒	▦	
	0,1	░	▓		▒	▦	
	0,2	▒	░	▦	▒	▒	▦

(B)

Si source: Aerosil Si/Al = 12, T = 140ºC, t = 3 days

		TEAOH/Si=0,2			TEAOH/Si=0,4		
		H_2O/Si			H_2O/Si		
		5	15	25	5	15	25
NaOH/Si	0,05	░	░	░	▒	░	
	0,1	▒	░	░	▒	▒	░
	0,2	▒	░	░	▒	▒	▒

	Amorphous
▒	BETA
░	ZSM-5
▨	BETA+ZSM-5
▧	ZSM12+Beta

Si source: Aerosil Si/Al = 12, T = 160ºC, t = 3 days

		TEAOH/Si=0,2			TEAOH/Si=0,4		
		H_2O/Si			H_2O/Si		
		5	15	25	5	15	25
NaOH/Si	0,05				▒	▧	
	0,1	░			▒	▒	▧
	0,2	▒	░	░	▒	▒	▒

(C)

Si source: MCM-41 Si/Al = 12, T = 140ºC, t = 3 days

		TEAOH/Si=0,2			TEAOH/Si=0,4		
		H_2O/Si			H_2O/Si		
		5	15	25	5	15	25
NaOH/Si	0,05	▒	░	░	▒	▒	░
	0,1	▨	░	░	▒	▒	░
	0,2	▒	░	░	▒	▒	▒

Si source: MCM-41 Si/Al = 12, T = 160ºC, t = 3 days

		TEAOH/Si=0,2			TEAOH/Si=0,4		
		H_2O/Si			H_2O/Si		
		5	15	25	5	15	25
NaOH/Si	0,05	░	░	░	▒	░	▒
	0,1	░	░	░	▒	▒	░
	0,2	░	░	░			▒

	Amorphous
▒	BETA
░	ZSM-5

(D)

Si source: BETA **Si/Al = 12, T = 140ºC, t = 3 days**

		TEAOH/Si=0,2			TEAOH/Si=0,4		
		H_2O/Si			H_2O/Si		
		5	15	25	5	15	25
NaOH/Si	0,05	▨	▨	▨	▨	▨	▨
	0,1	▨	▨	▨	▨	▨	▨
	0,2	▨	▨	▨	▨	▨	▨

Si source: BETA **Si/Al = 12, T = 160ºC, t = 3 days**

		TEAOH/Si=0,2			TEAOH/Si=0,4		
		H_2O/Si			H_2O/Si		
		5	15	25	5	15	25
NaOH/Si	0,05	▨	▨	▨	▨	▨	▨
	0,1	▨	▨	▨	▨	▨	▨
	0,2	▨	▨	▨	▨	▨	▨

▨	BETA

Figure S3: Thermogravimetric analysis (TGA) of as-prepared CHA-1 sample

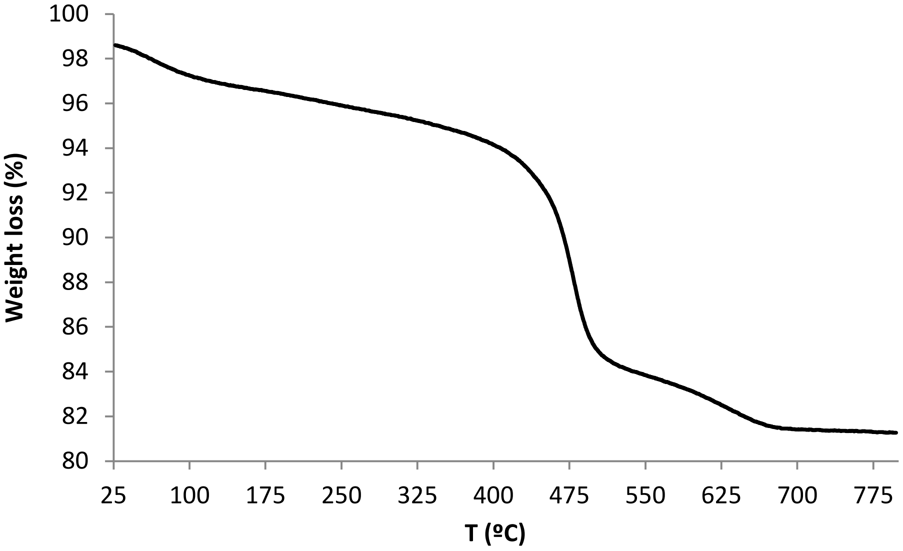

Figure S4: N_2 adsorption isotherm of calcined CHA-1 sample

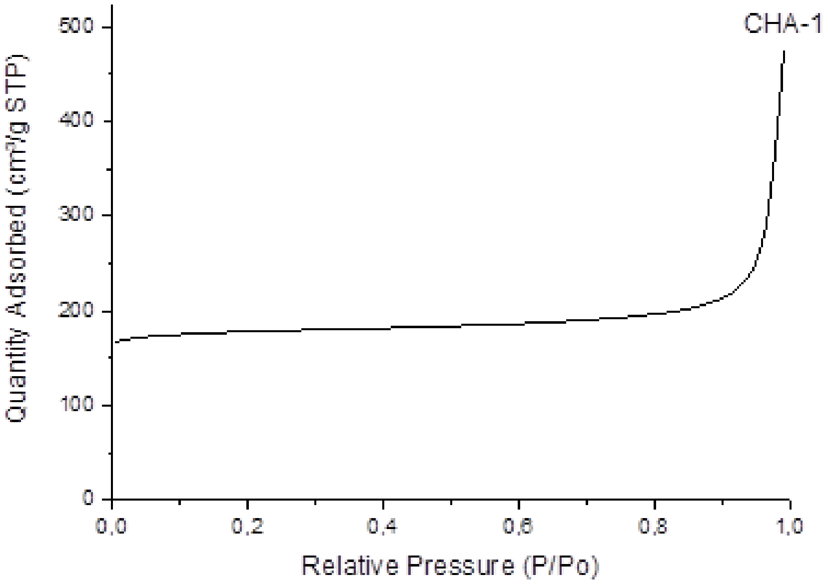

Figure S5: SEM images of CHA-1 sample

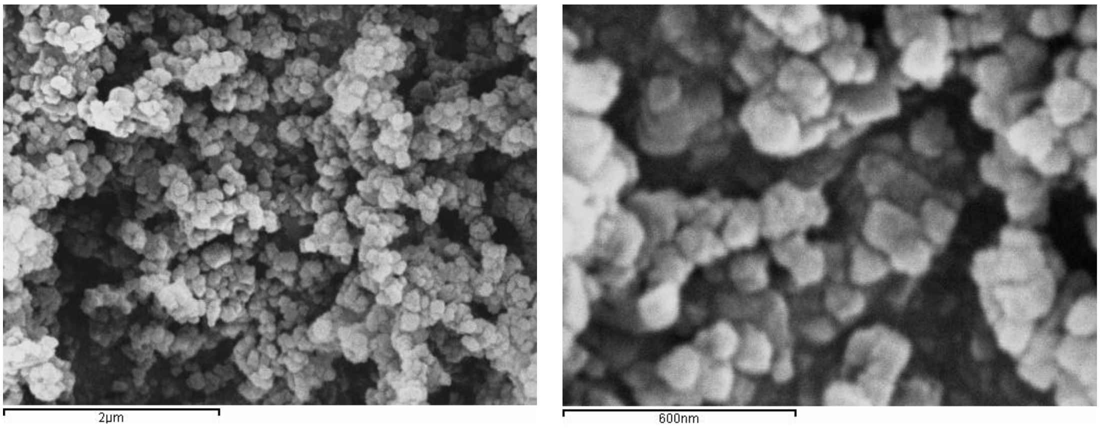

Figure S6: ^{27}Al BD MAS NMR spectra of as-prepared and calcined CHA-1 materials

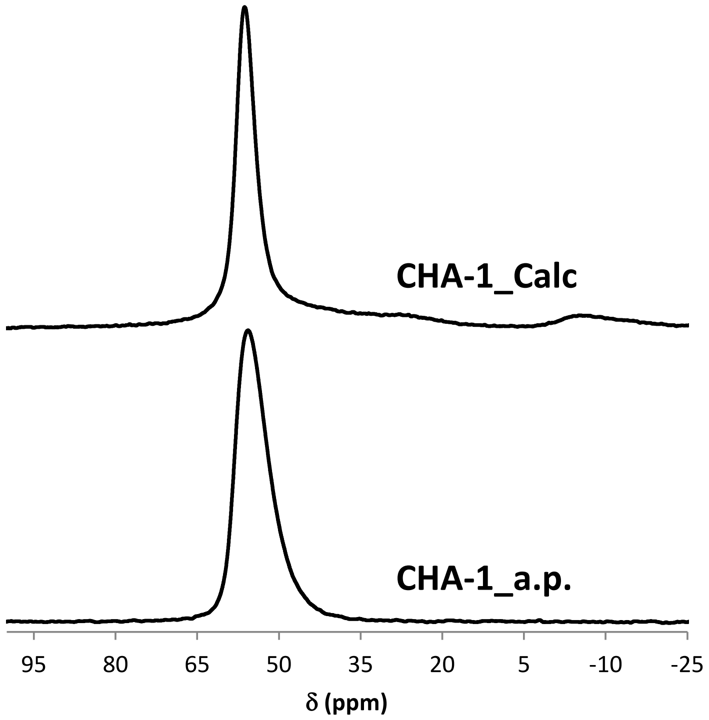

Figure S7: UV-Vis spectrum of the as-prepared Cu-CHA-2 material

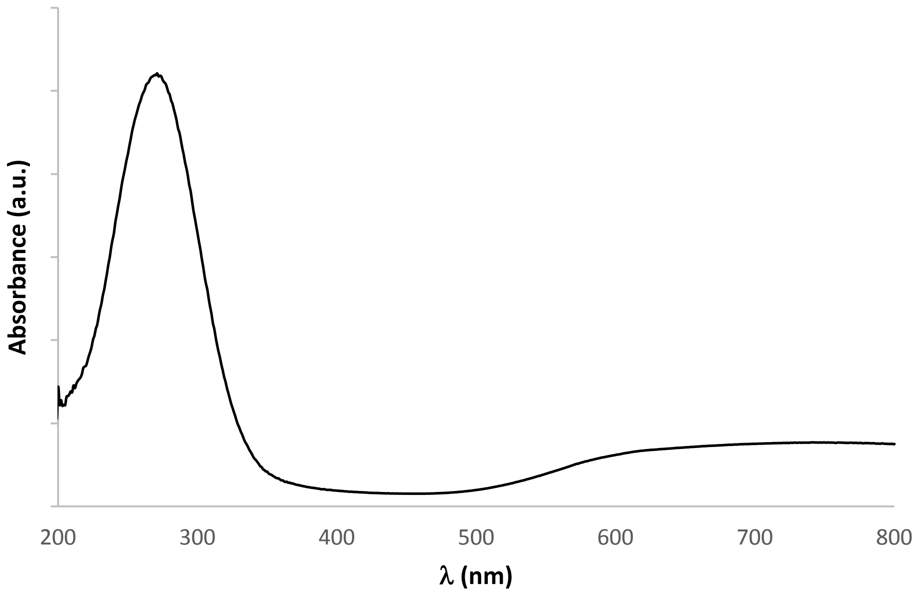

Table S1: ICP analyses of the zeolitic samples

Sample	Si/Al	Na/(Si+Al)	Cu/Al	%wt Cu
CBV720 (USY)	10.5	0.00	---	---
CHA-1	8.5	0.03	---	---
Cu-CHA-1	8.5	0.00	0.20	2.2
Cu-CHA-2	10.3	0.03	0.46	4.1