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

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In the last years, small pore zeolites containing large cavities in their structures have been reported as efficient catalysts for particular chemical processes, such as methanol to olefins (MTO) and selective catalytic reduction (SCR) of NOx.[1] From the large list of small pore zeolites described in the literature, chabazite (designated as the structure type code CHA) is a very atractive material.[1] CHA is a three-dimensional small pore zeolite with pore openings of 3.8x3.8 Å and large ellipsoidal cavities of 8.35 Å (see Figure 1).[2] In addition to these large cavities, the CHA framework also contains the presence of specific secondary building units (SBUs), named double six member-rings (D6Rs, see Figure 1).

CHA is a natural zeolite presenting the following composition $Ca_6Al_{12}Si_{24}O_{72}$. However, the application of CHA has required the synthesis of the high-silica silicoaluminate (SSZ-13)[3] and silicoaluminophosphate (SAPO-34)[4] polymorphs. Although SAPO-34 has been applied as industrial catalyst for the MTO process,[5] there is interest to further develop silicoaluminate counterparts.[6]

The preferred synthesis procedure to prepare the high silica silicoaluminate SSZ-13 requires the use of an expensive organic structure directing agent (OSDA), as the trimethyladamantammonium (TMAdA) cation.[3] There is, consequently, much incentive to reduce the manufacturing costs, by finding less expensive OSDAs.[7] Therefore, several research groups, mainly from industry, have attempted the synthesis of the SSZ-13 zeolite using alternative and less expensive OSDAs. TMAdA has been used in combination with benzyltrimethylammonium (BTMA),[8] or tetramethylammonium (TMA),[9] to replace some of the more expensive OSDA with a less selective but less-expensive pore filler (BTMA and TMA). On the other hand, the use of less-expensive single OSDA molecules for the synthesis of the SSZ-13 zeolite, such as BTMA,[10] N-alkyl-1,4-diazabicycle[2.2.2]octane cations,[11] diverse cycloalkylammonium cations,[12] N,N-dimethylpiperidinium,[13] and choline,[14] has also been recently proposed. However, the preparation of some of these organic molecules still remains fairly expensive, or the crystalline materials are obtained with low solid yields.

The synthesis of the CHA zeolite under OSDA-free synthesis conditions has also been attempted,[15] but the Si/Al ratios achieved, so far, are very low (below 4), resulting in

catalysts with poor acidity and hydrothermal stability, or their micropore volume is low, or the yields obtained are below 50%.

We have attempted to rationalize the potential use of less expensive OSDAs for the synthesis of high silica CHA. For doing that, we have considered the organic structure directing agents used for the preparation of the silicoaluminophosphate SAPO-34 material in the literature. One of the preferred organic molecules to synthesize SAPO-34 is the comercially available tetraethylammonium (TEA) cation.[16] However, when TEA is used as OSDA for the synthesis of high-silica silicoaluminate materials, Beta zeolite is mostly achieved under very broad synthesis conditions.[17] This made us to think on the dominant role of TEA for nucleation of Beta versus chabazite, and the necessity to modify the kinetics of the nucleation to increase the relative rate of formation of chabazite versus Beta by introducing in the synthesis, a silica source with building units that are not in the BEA structure. The first obvious choice was to introduce chabazite seeds together with LUDOX and aerosil as silica sources. Unfortunately, the results presented in Figure S1 indicate that chabazite was not obtained, at least with high yields, but Beta was still the predominant phase.

At this point, we noticed that faujasite (USY) zeolite has been succesfully used as a silica source to synthesize some 8-ring pore zeolites, such as SSZ-13 (CHA)[18] and levyne (LEV),[19] using TMAda and N-methylquinuclidinium as OSDAS, respectively. Furthermore, all these zeolite have in their structure a common building unit with the FAU structure, i. e. the D6Rs. Thus, in a similar way as we found that the introduction or formation of double-4-rings (D4Rs) in solution directed towards the synthesis of zeolites with D4Rs in their structures by strongly increasing their rate of nucleation,[20] we thought that the introduction of faujasite (USY) as silica source and its possibility to supply D6R subunits, could improve the kinetics of formation of chabazite versus Beta. In fact, the introduction of a pre-crystallized zeolite as silicon and aluminum source for attempting the synthesis of a different zeolite has been described as an efficient method, since the involved nucleation/crystallization processes can be strongly modified compared to conventional amorphous aluminosilicate gels.[21] This fact could be explained by the presence of ordered small nanoparts by decomposition/dissolution of the former crystalline zeolite that can result in the formation of different crystalline structures.[18,19,22]

Here, the efficient synthesis of high-silica CHA zeolite using TEA as OSDA and high-silica USY as silicon and aluminum source will be shown. The catalytic properties of the Cu-exchanged CHA zeolite will be evaluated for the selective catalytic reduction (SCR) of NOx. In addition, the direct synthesis of the Cu-containing CHA using a combination of TEA and a Cu-complex (Cu-tetraethylenepentamine, Cu-TEPA) as OSDAs will also be described.

To attempt the synthesis of CHA zeolite using TEA as OSDA and USY as Si and Al source, a broad experimental design has been developed where the following synthesis variables have been studied: TEAOH/Si, H_2O/Si, NaOH/Si and crystallization temperature. The values for TEAOH/Si, H_2O/Si and NaOH/Si molar ratios were [0.2, 0.4], [5, 15, 25], and [0.05, 0.1, 0.2], respectively. The syntheses were carried out at 140 and 160ºC for 3 days under static conditions.

As it can be seen in Figure 2, CHA is preferentially formed under high NaOH/Si (0.2) and TEAOH/Si (0.4) ratios regardless crystallization temperature and water content. CHA is also crystalized under particular conditions when the amount of TEAOH is reduced in the synthesis media (TEAOH/Si = 0.2, see CHA-1 sample in Figure 2). On the other hand, the formation of Beta zeolite as pure phase or forming part of a mixture with CHA is observed when the syntheses are performed under lower NaOH/Si ratios (0.05 and 0.1, see Figure 2). Finally, some experiments performed using low NaOH/Si and TEAOH/Si ratios show the presence of the former USY material (see FAU in Figure 2). This fact could be explained by the low amount of mobilizing agent in the synthesis gel that is not enough to dissolve-mobilize the initial USY used as zeolitic precursor.

As it is shown in Figure 2, one of the key parameters to control the synthesis of CHA using USY as zeolitic precursor is the amount of the mobilizing agent in the synthesis media. Indeed, the crystallization of CHA is highly favored under higher OH/Si ratios. Nevertheless, if the concentration of OH in the synthesis media is too high, part of the Si and/or Al sources would remain in solution as silicate or aluminate species under those high pHs, resulting in a severe decrease of the zeolite yield. In this sense, CHA-1 zeolite shows the highest solid yields (above 85%). This can be explained by the fact that CHA-1 has been synthesized with the lowest content of TEAOH, and thus, with moderate amount of mobilizing agent in the synthesis media. Interestingly, the

synthesis of CHA using the lowest content of OSDA is important to reduce the global cost of the catalyst preparation.

For comparison purposes, other Si and Al sources have been tested under similar synthesis conditions using TEA as OSDA (see Figure S2 in Supplementary Material). The use of colloidal silica, fumed silica, MCM-41 or Beta zeolite, results in the preferential crystallization of Beta and ZSM-5 zeolites (see Figure S3 in Supplementary Material). These crystalline zeolites have been broadly described in the literature using TEA or related alkylammonium cations as OSDAs. It is worth noting that the crystallization of the CHA zeolite is not observed under the extensively evaluated synthesis conditions, revealing the pivotal role of using high-silica USY zeolite as Si and Al crystalline precursor.

The powder X-Ray diffraction pattern (PXRD) of the as-prepared CHA-1 sample shows the presence of CHA zeolite as pure phase (see Figure 3), indicating the complete absence of other crystalline phases, including the crystals of USY that were used as zeolitic precursor.

Thermogravimetric analysis (TGA, see Figure S3 in Supplementary Material) and elemental analysis (1.69 %wt N, 11.03 %wt C) of the as-prepared CHA-1 reveal that there are 3.2 TEA molecules per unit cell, corresponding to one TEA molecule per CHA cavity. This result indicates the excellent organic directing effects of TEA for stabilizing CHA cavities.

The crystalline structure of CHA-1 material remains stable after being calcined in air at 580ºC for 5 hours (see the PXRD pattern of the calcined CHA-1 sample in Figure 3). The micropore volume of the calcined CHA-1 is 0.26 cm^3/g, and its crystallite size is 0.1-0.2 μm, (see Figure S4 in Supplementary Material).

Chemical analyses of the CHA-1 sample reveal Si/Al and Na/Al molar ratios of 8.5 and 0.3, respectively (see Table S1 in Supplementary Material), being the Al in tetrahedral coordination as indicated by ^{27}Al BD MAS NMR spectroscopy (see Figure S5 in Supplementary Material).

CHA materials containing extra-framework Cu^{2+} species have been described as very efficient catalysts for the SCR of NOx.[1] In our case, Cu^{2+} has been introduced by cation exchange at 2.2%wt (see Cu-CHA-1 in Table S1 in Supplementary Material) and calcined as described in the experimental section.

The catalytic activity of the Cu-exchanged CHA material has been evaluated for SCR of NOx using NH_3 as reductor. The reaction has been performed using a feed composed by 500 ppm of NO, 500 ppm of NH_3, 5% of water and 7% of O_2 in a wide range of reaction temperatures (170-550ºC), with a very high gas hourly space velocity of 450,000 ml/h.g_{cat}. Cu-CHA-1 catalyst shows high catalytic activity, achieving NO conversion values above 90% between 200 and 500ºC (see Figure 4). After steaming the sample at 750ºC for 13 hours, the crystallinity of the sample remains intact (see PXRD pattern of Cu-CHA-1_HT750 in Figure 3), and most of the original catalytic activity of the fresh sample is preserved (see Cu-CHA-1_HT750 in Figure 4).

We have also made the one-pot synthesis of Cu-CHA catalysts [23] using TEA and Cu-TEPA as OSDAs and USY as zeolitic precursor (see experimental section for synthesis details).

Following this direct synthesis methodology, a crystalline Cu-containing CHA sample has been obtained (see PXRD pattern of Cu-CHA-2 in Figure 3). Cu-TEPA complex is retained intact after crystallization within the pores of the CHA crystals, as reveals the presence of the single band centered at 270 nm in the UV-Vis spectrum of the as-prepared Cu-CHA-2 material (see Figure S6 in Supplementary Material). At this point, the required cationic copper extra-framework species for De-NOx applications can be easily produced by calcining the as-prepared Cu-CHA-2 sample to remove the occluded organic moieties. Calcined Cu-CHA-2 catalyst shows high catalytic activity for SCR of NOx, with NO conversions analogous to those achieved with the Cu-exchanged CHA catalysts (see Figure 4).

These preliminary results would suggest that the low-cost methodologies described here, both Cu-exchanged and "one-pot", to synthesize Cu-containing CHA catalysts using TEA as OSDA could be competitive and attractive for industrial applications, such as NH_3-SCR of NOx.

Figure 1: Crystalline structure of CHA zeolite

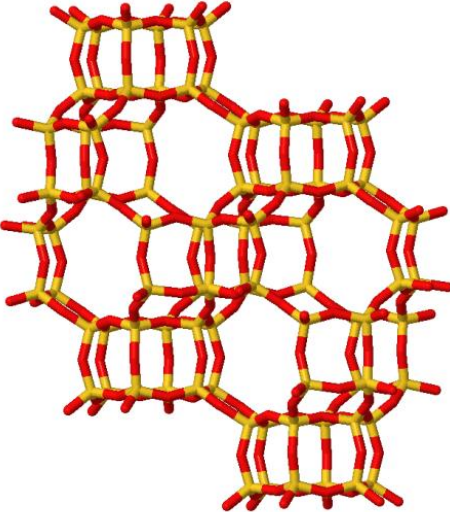**Figure 2: Phase diagram achieved using TEA and USY zeolite as OSDA and zeolitic precursor, respectively.**
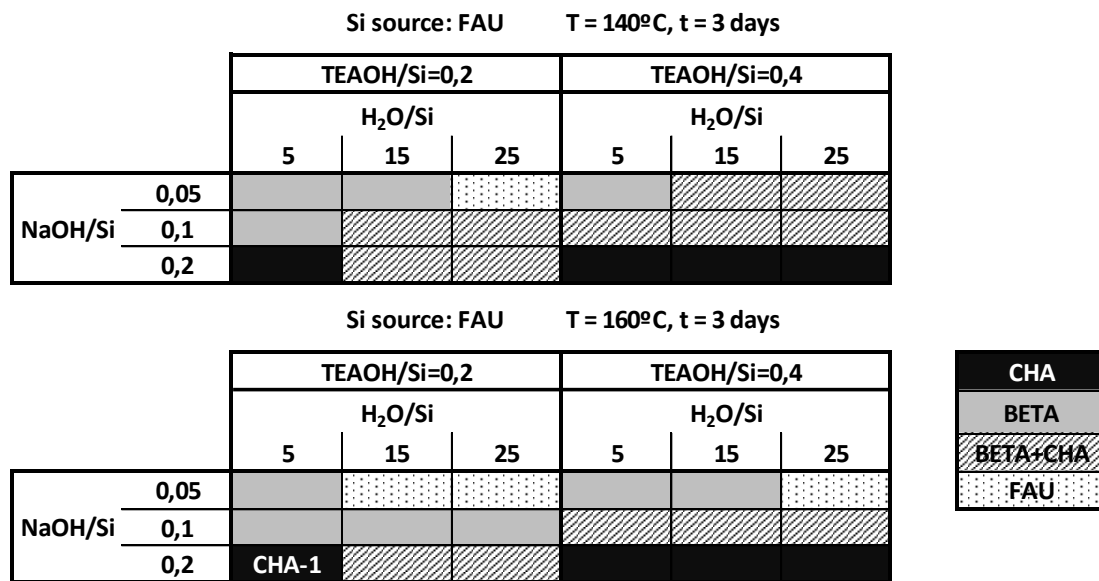
Si source: FAU   T = 140ºC, t = 3 days

		TEAOH/Si=0,2			TEAOH/Si=0,4		
		H₂O/Si			H₂O/Si		
		5	15	25	5	15	25
NaOH/Si	0,05						
	0,1						
	0,2						

Si source: FAU   T = 160ºC, t = 3 days

		TEAOH/Si=0,2			TEAOH/Si=0,4		
		H₂O/Si			H₂O/Si		
		5	15	25	5	15	25
NaOH/Si	0,05						
	0,1						
	0,2	CHA-1					

Legend
CHA
BETA
BETA+CHA
FAU

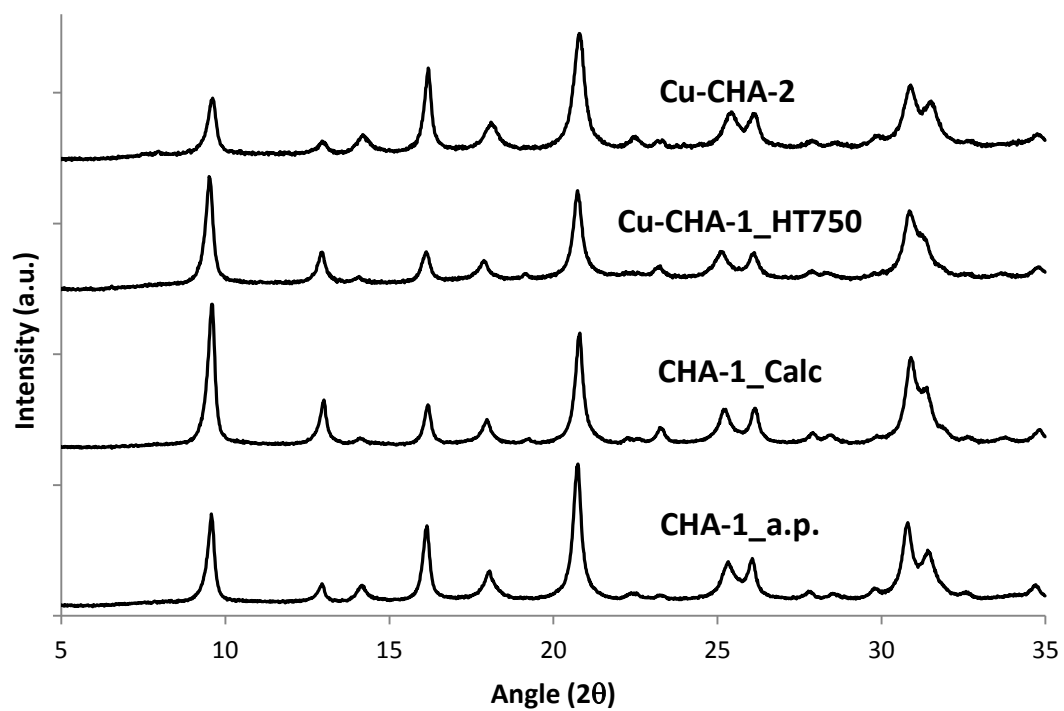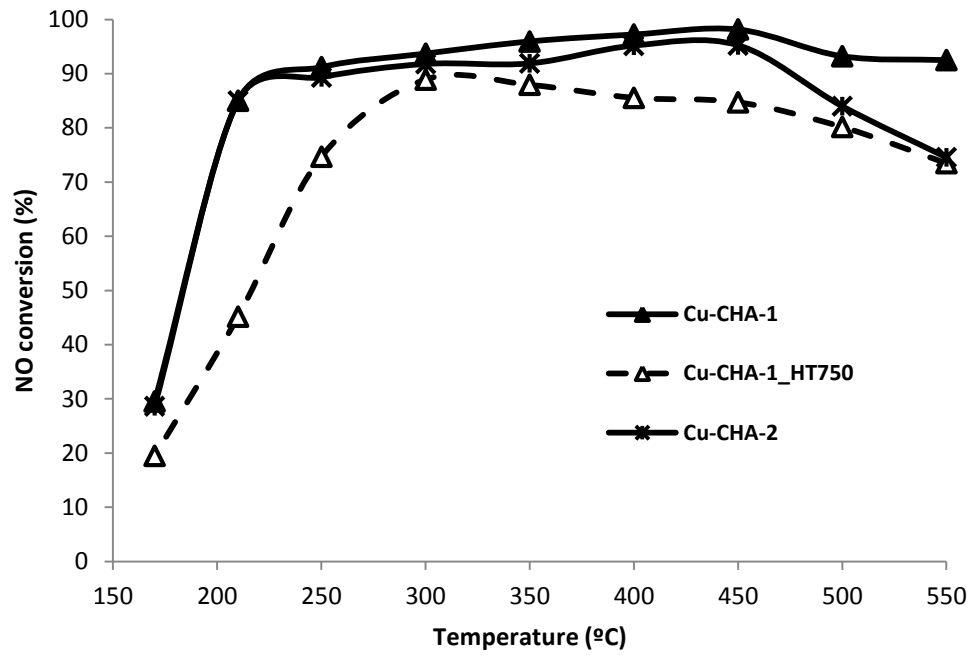**Figure 3: PXRD patterns of CHA materials**

Figure 4: Catalytic activity for the NH$_3$-SCR of NOx reaction of the different Cu-CHA materials synthesized using TEA as OSDA under severe reaction conditions in presence of water and very high space velocity (450,000 ml/h.g$_{cat}$)

Supplementary Material

Experimental

1.- Synthesis

<u>Synthesis of aluminosilicate zeolites using tetraethylammonium as OSDA and USY zeolite as silicon and aluminum sources</u>

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 SiO2/Al2O3=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 413 or 433K for 7 days under static conditions. The solid product was recovered by filtration, washed with water and dried at 373K.

For the particular case of the optmized CHA-1 material, the final gel composition for its preparation was SiO2 / 0.047 Al_2O_3 / 0.2 TEAOH / 0.2 NaOH / 5 H_2O using CBV-720 as silicon source. The crystallization was conducted hydrothermally at 433K for 7 days under static conditions. The solid product was recovered by filtration, washed with water and dried at 373K. Finally, the solid was calcined in air at 823K for 4h.

It is important to note that CHA-1 material has been used as the CHA seeds for the experiments reported in Figure S1.

<u>Synthesis of aluminosilicate zeolites using tetraethylammonium as OSDA and different sources of Si and Al</u>

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 413 or 433K for 7 days under static conditions. The solid product was recovered by filtration, washed with water and dried at 373K.

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 followed 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 source. The gel was transferred to an autoclave with a Teflon liner, and heated at 433K under static conditions for 7 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° 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 (A) and Aerosil (B)] and seeds of CHA (10%wt)

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

Si-source		TEAOH/Si=0,2			TEAOH/Si=0,4		
		H$_2$O/Si			H$_2$O/Si		
		5	15	25	5	15	25
	LUDOX	BETA			BETA	BETA	BETA+CHA
	Aerosil	BETA			BETA	BETA	BETA+CHA

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
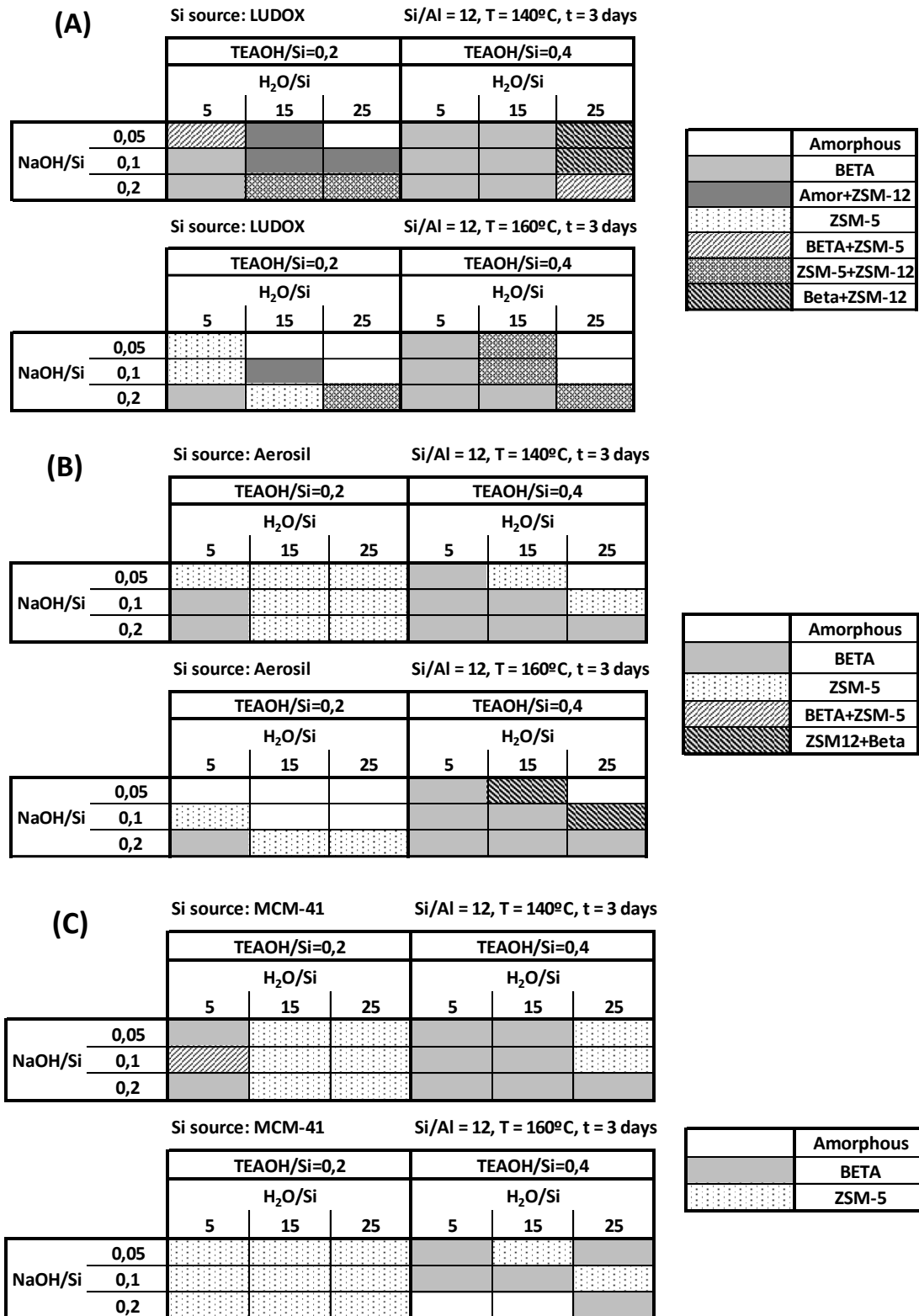
(D)

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

		TEAOH/Si=0,2			TEAOH/Si=0,4		
		H₂O/Si			H₂O/Si		
		5	15	25	5	15	25
	0,05						
NaOH/Si	0,1						
	0,2						

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

		TEAOH/Si=0,2			TEAOH/Si=0,4		
		H₂O/Si			H₂O/Si		
		5	15	25	5	15	25
	0,05						
NaOH/Si	0,1						
	0,2						

	BETA

Figure S3: Thermogravimetric analysis (TGA) of as-prepared CHA-1 sample
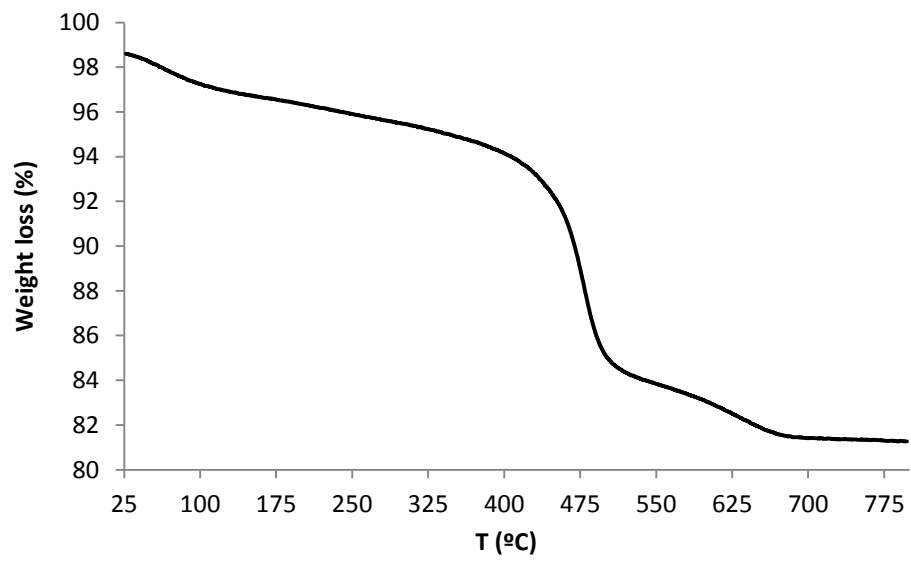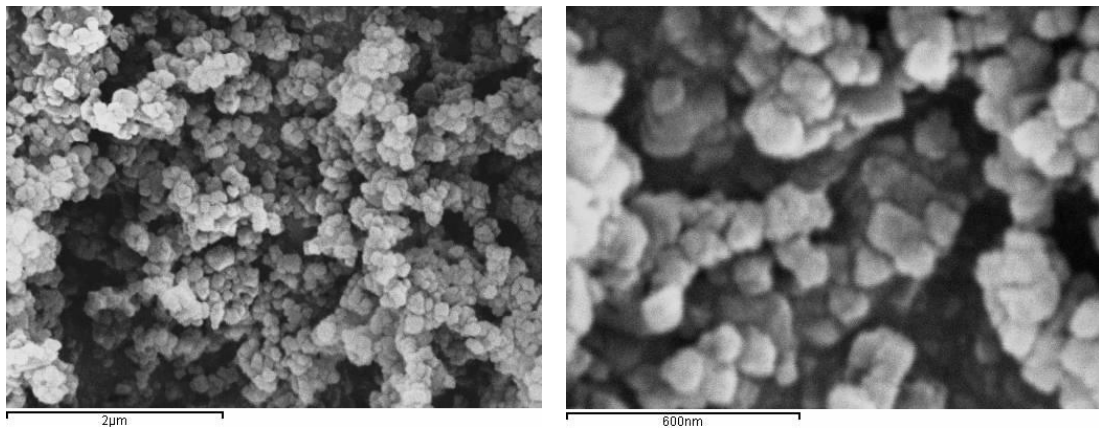
Figure S4: SEM images of CHA-1 sample

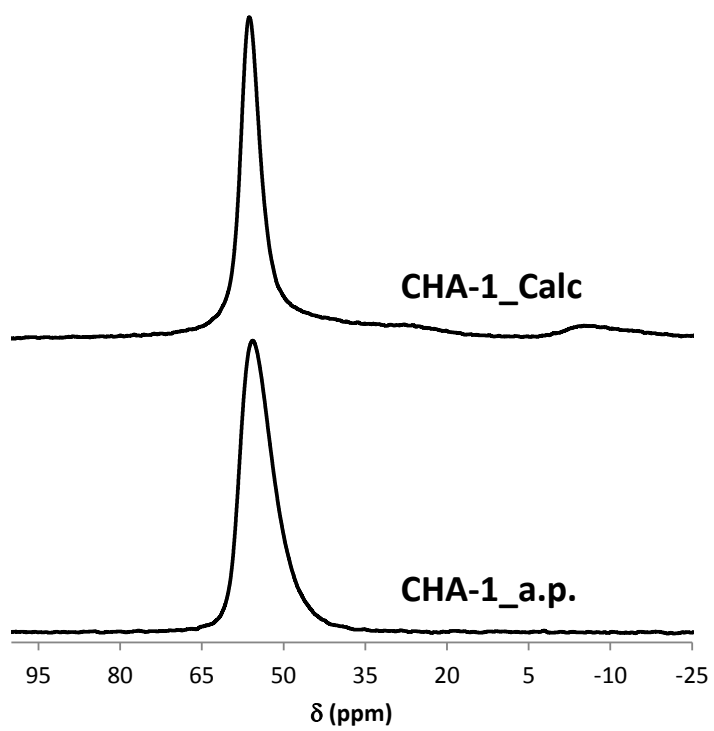**Figure S5: ^{27}Al BD MAS NMR spectra of as-prepared and calcined CHA-1 materials**

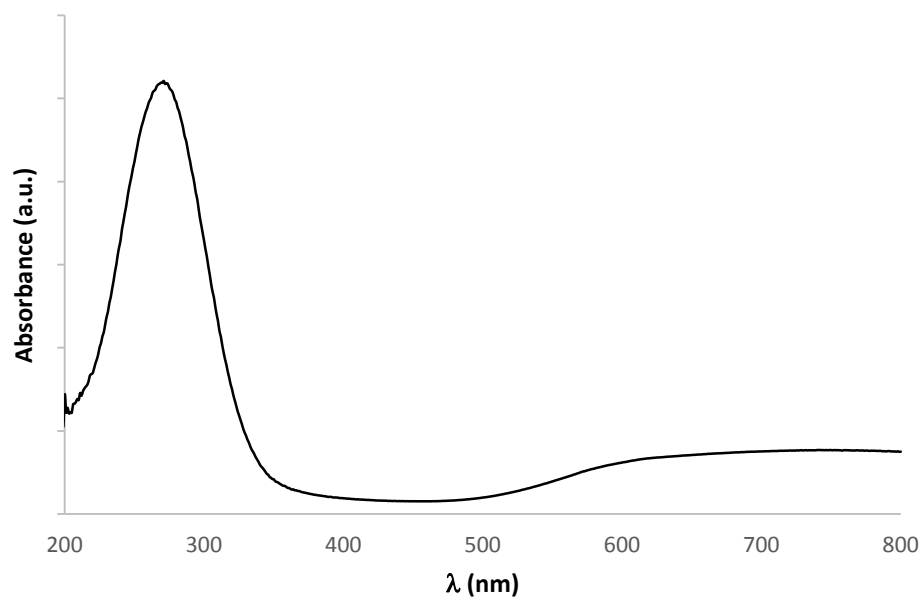**Figure S6: UV-Vis spectrum of the as-prepared Cu-CHA-3 material**

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

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