

In-containing BEA zeolite for selective catalytic reduction of NO_x Part I: Synthesis, characterization and catalytic activity

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Abstract

In this work we show the effect of preparation method of BEA zeolite, the indium loading method, on the performance for NO_x -SCR with methane in presence of oxygen. Temperature programmed ammonium desorption (TPAD), XRD, BET, NMR-MAS of ^{27}Al and Fourier transformed infrared spectroscopy (FTIR) of pyridine adsorbed on the samples, allowed us to correlate the catalytic activity with the nature of the active sites of the catalysts. The catalyst activity is affected by strong Brønsted sites and the type of In precursor (InCl_3 and In_2O_3) and is influenced by the indium loading methods. The ion exchange in liquid phase method results in a higher activity than ion exchange in solid phase method.

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Keywords: In-BEA; Synthesis; Characterization; NO_x -SCR

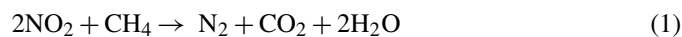
1. Introduction

The nitrogen oxides reduction is a problem that the environmental catalysis still tries to solve. Different approaches in the search of solutions exist to eliminate or to diminish the transmission of polluting agents at compatible levels with the established ones in the norms, being able in general to attack the problem of two ways that can be complementary: (a) prevention in the generation of the polluting agent, (b) elimination of the polluting agent already generated by the process. The first step is framed in the denominated clean technologies; the second is to transform the polluting effluents into innocuous substances or with smaller risk. Thus, for this problematic, the processes can be grouped in three general lines of work: minimization of the production of NO_x ; direct decomposition of NO to $\text{N}_2 + \text{O}_2$, and selective catalytic reduction (SCR). In this way the catalytic processes have great relevance, considering that the catalysis has played and will continue playing the most important role in the reduction of polluting agents and within these the based ones on different zeolites.

First of these three lines, it presents great technological and economic difficulties to face on the part of the companies. Second, it consists of the design of a catalyst able to accelerate the reaction of direct decomposition of NO to N_2 and O_2 . This reaction is thermodynamically favored. Nevertheless, from the kinetic point of view it is very difficult to disturb NO only thermally or by means of the use of catalysts. In this last case, one of the central problems is the loss of activity by fouling due to the production of oxygen in the decomposition. From the discovery of Iwamoto et al. [1], demonstrating that the Cu-ZSM-5 zeolite presents a great activity for the direct decomposition of NO , was generated a great enthusiasm in the international community of catalysis [2–4]. But, when verifying it, even in the most propitious conditions, the activity is too low for its commercial use; the interest by this system has been decreasing. Later this catalyst was used in the selective catalytic reduction with hydrocarbons (HC-SCR) in different catalytic systems with excess of oxygen [5–8]. The third line of work, also consists of a catalytic process, which uses hydrocarbons (olefins or paraffin of low molecular weight) like reducing agents of NO_x ; but the cost is elevated in the cases in that these agents are not presents in exhaust gases [5,6]. Li and Armor [9] were the pioneers in reporting Co-ZSM-5 as affective catalyst for the selective reduction of NO_x in the presence of excess of oxygen and methane like reducer. Kikuchi

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and Yogo [10] propose a preponderant role in the acceleration of the reduction of NO_x with methane, of gallium and indium species on H-ZSM-5. Gallium or indium supported on zeolites were discovered to be better suitable for CH_4 -SCR than copper or iron, which favor the direct oxidation of CH_4 to CO_2 [10–12]. Indium zeolite catalysts have been obtained by loading of the zeolite from aqueous indium salt solution or by mixing of In_2O_3 and zeolite [11,13]. A reaction mechanism for SCR of NO_x by methane was proposed, which starts with the oxidation of NO to NO_2 on Brønsted-acid sites followed by reaction of NO_2 and CH_4 on $(\text{InO})^+$ species (Eq. (1)).



Nevertheless, a minor attention has been paid to In-containing zeolites as active material, although these are known as promising catalysts for the SCR with methane [9,10]. In a recent work, Schmidt and co-workers [14], showed the influence of the preparation mode of zeolite with In as active species for selective reduction of NO by hydrocarbons, indicating by their spectroscopic studies different and distinguishing intra- and extra-zeolite In species, specially by XAFS techniques.

The potential of zeolites MFI and MOR promoted by In and Ce as catalysts for the SCR of NO_x by methane and propane was studied by Berndt et al. [12], they demonstrated the catalytic function of different indium species ($(\text{InO})^+$, In_2O_3 cluster) and their cooperation with ceria in the composite catalyst. The primary role of the CeO_x promoter is to catalyze the oxidation of NO to NO_2 . Probably, NO_2 reacts with methane on Lewis acidic and redox-active $(\text{InO})^+$ species, but the further reaction of the intermediate formed needs the presence of residual Brønsted-acid sites. Furthermore, combining of methane and propane as reductants opens an opportunity to broaden the ‘temperature window’ for the SCR of NO_x . Different influence of hydrothermal ageing was obtained with methane and propane, respectively, as reducing agent [12,13].

Kikuchi and co-workers [15,16] compared the catalytic activities of In/HZSM-5 prepared by ion exchange and In_2O_3 /HZSM-5 prepared by physically mixing HZSM-5 with In_2O_3 , and found that In/HZSM-5 and In_2O_3 /HZSM-5 were equally active in the CH_4 -SCR of NO_x . Richter et al. [17] reported that In/H-mordenite catalysts prepared by ion exchange or impregnation displayed similar activities, and they showed that the In locating on the ion exchange positions had a strong Lewis acid character. Ren et al. [18], have found that the activity of the In/HZSM-5 prepared by impregnation of HZSM-5 with the solution of $\text{In}(\text{NO}_3)_3$ showed high activity for CH_4 -SCR of NO. Recently, extensive efforts have been made to improve the activity and selectivity of In/HZSM-5 [17–19]. Ogura et al. found that the addition of a noble metal, especially iridium, to In/HZSM-5 could enhance NO conversion to N_2 remarkably [16], and they suggested that the reaction proceeds in two stages, namely NO is first oxidized to NO_2 on Ir, and then NO_2 is reduced to N_2 by CH_4 on InO^+ [16]. Ren et al. [19], using colloidal alumina enhance the activity of In/HZSM-5. Two kinds of indium-sites in In/HZSM-5/ In_2O_3 showed remarkable activity for CH_4 -SCR of NO_x [18]. Indium has a role to enhance the

adsorption of NO_x species at reaction conditions. Intrazeolite indium oxo-species $(\text{InO})^+$ are active CH_4 -SCR sites [19–21].

Maunula et al. [22] reported that indium on protonated H-ZSM-5 showed a higher activity in dry conditions while indium on unprotonated ZSM-5 with a high loading of 7.3% prepared by ion exchange had a higher activity in the presence of 8% water. NO_2 in feed promoted the methane oxidation and NO_x reduction. In situ Fourier transformed infrared spectroscopy (FTIR) analysis revealed on In/ZSM-5 the presence of inhibiting compounds at lower temperatures and many carbonaceous surface compounds. It is proposed that the formation of NO_2 , partially oxidized methane surface derivatives and actual surface reductants containing N–C or N–H bindings are crucial in NO reduction. Intrazeolitic InO^+ was proposed to be the active catalytic site in NO reduction. Free In_2O_3 , detected by XRD and XPS, has possibly a promoting effect on the reactions. The adsorbed H_2NCO intermediate, formed in the reaction between NO_2 and partially oxidized methane, was proposed to act as an actual NO reductant in the reaction mechanism.

Reductive solid-state ion exchange (RSSIE) has recently proved to be a promising method for the post-synthesis modification of zeolites. However, until now its application seems to be limited to only a reported few elements. This method was first reported by Kanazirev et al., who found that gallium [23,24] and indium [25] are incorporated into H-ZSM-5 when mechanical mixtures of this zeolite with Ga_2O_3 or In_2O_3 are heated in hydrogen at 547–647 °C. More recently, RSSIE of univalent indium ions was studied in more detail [26–28]. So far, no other elements existing in different oxidation states were reported to be introduced into zeolite structures in form of low-valence cation by RSSIE.

Sowade et al. [29,30] have prepared In-ZSM-5 catalysts by different routes (aqueous ion exchange at different pH values; solid-state ion exchange, sublimation, and transport reaction, with an InCl_3 indium source) and compared with respect to their catalytic behaviour in the SCR (1000 ppm NO, 1000 ppm methane, 2% O_2 in He, at 30,000 h^{-1}) to elucidate the origin of differing NO conversion-temperature characteristics observed with the In-ZSM-5 catalyst system. On the basis of structural information available from EXAFS and XPS studies they found intrazeolite indium oxo-species exclusively or coexisting with extrazeolite indium oxo-aggregates. The results confirmed that intrazeolite indium oxo-species are active SCR sites. Their catalytic properties depend on details of the coordination environment. The presence of extrazeolite InO_x species is hardly reflected in the SCR activity but induces unselective methane activation. In addition, they observed the complete failure of an In-silicalite-1 catalyst in NO reduction despite considerable methane activation capability indicated a crucial role of Brønsted acidity for the SCR over In-ZSM-5 catalysts [30].

We recently [31] supported the idea that the activation of methane is initiated by NO_2 and NO_3^- chemisorbed species on InO^+ sites of the In-ZSM-5 zeolite. In this work, we show the effect of zeolite catalyst topology and the nature of active species of In-sites by ion exchange in liquid phase (IELP) and ion exchange in solid phase (IESP) on BEA zeolite synthesized by a benefit sol-gel method [32].

In this contribution we also present the performance of a synthesized thermally stable In-HBEA zeolite, and report on the procedure of the introduction of indium cation into zeolite BEA. The indium was incorporated by IELP and IESP (similar to the above denoted as RSSIE), with special attention being paid to the chemical nature and the redox behaviour of the incorporated cationic indium species. Temperature programmed ammonium desorption (TPAD), XRD, NMR, BET and FTIR of pyridine allowed us to correlate the catalytic activity with the nature of the active sites of the catalysts. The results shown here, about the In-HBEA zeolite synthesized by sol–gel technique and its application to NO_x -SCR, are one of the first reported in literature.

2. Experimental

2.1. Catalysts preparation

BEA zeolite was prepared using the following reactants: tetraethylorthosilicate (TEOS), as the source of silicon; sodium aluminate, as the source of aluminum and tetraethylammonium hydroxide as template. The technique procedure is described by the next steps:

Step a: TEOS (hydrolyzed with HCl for 1 h) and Al source in water were added to the resultant solution at 0 °C. The clear solution obtained was stirred for 20 min.

Step b: The final solution of step a, is converted into a solid co-gel by addition of the corresponding template at room temperature. The xerogel obtained was dried at 110 °C overnight.

Step c: The xerogel obtained in step b, was impregnated with the adequate template solution by wetness impregnation. The incipient wetness $\text{SiO}_2/\text{Al}_2\text{O}_3$ was charged in a Teflon-lined autoclave and crystallized at 150–180 °C for 30–100 h. The final product was filtered, washed with distilled water, dried at 110 °C, followed by a post-synthesis treatments: the sample was calcined at 500 °C for 12 h under nitrogen flow of 10 ml/min and 2 °C/min from 100 °C, then the samples were calcined in air at 500 °C for 8 h. The ammonium form of the catalyst was prepared by ion exchange of Na-BEA with ammonium chloride 1 M at 80 °C for 40 h. The H-BEA zeolite was obtained after the thermo-elimination of ammonium under 20 ml/min of N_2 flow from 100 to 500 °C at 2 °C/min, and then calcined in air at 500 °C for 6 h. The Si/Al molar ratio was 23 for H-BEA zeolite. The Si/Al molar ratio was determined by ICP. The In content was evaluated by PAC (see Part II).

2.1.1. Incorporation of In on BEA zeolite

2.1.1.1. Ion exchange in liquid phase (IELP). The In-HBEA form of the catalyst was prepared by ion exchange of NH_4 -BEA with an aqueous solution of InCl_3 (diluted by in excess) at 80 °C during 24 h with magnetic stirring. Later, the sample was filtered, washed and dried at 90 °C for 10 h. The sample was calcined at 500 °C for 12 h under oxygen flow of 10 ml/min and 2 °C/min from 100 °C, and then the sample was calcined at 500 °C during 12 h in air. The Si/Al molar ratio was 23. The cata-

lyst obtained is In-HBEA denoted as: sample A with a 2% (w/w) of In.

2.1.1.2. Ion exchange in solid phase (IESP). The NH_4 -BEA was mixed with In_2O_3 (in sufficient amount to incorporate an atom of In by each Al atom) using a planetary mill at average speed during 20 min. The obtained preparation was calcined at 500 °C under oxygen flow of 10 ml/min and 2 °C/min from 100 °C and then calcined during 12 h at 500 °C in air. The samples obtained are indicated in the present work according the post treatments, as—sample AM: as made (In_2O_3 -HBEA, 2% (w/w) of In with Si/Al molar ratio of 23); sample B: AM sample reduced under H_2 flow of 5 ml/min and 2 °C/min from 100 to 500 °C, holding this temperature during 12 h, then it is oxidized at 500 °C under oxygen flow of 10 ml/min and 2 °C/min from 100 °C and calcined during 12 h at 500 °C (In-HBEA, 2% (w/w) of In, with Si/Al molar ratio of 23); sample C: AM sample reduced under H_2 atmosphere from 100 to 300 °C and then oxidized at 500 °C (following the same procedures described for sample B, obtaining In-HBEA catalyst with 2% (w/w) of In and Si/Al molar ratio of 23).

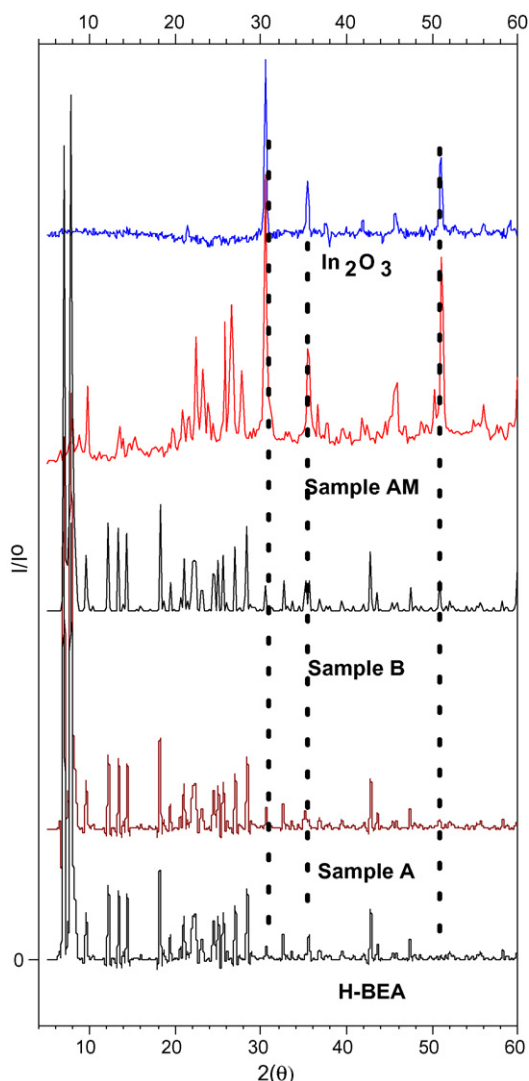


Fig. 1. XRD pattern of H-BEA and In-HBEA samples and In_2O_3 .

2.2. Catalytic activity

The studies on the catalytic activity were carried out using a flow reactor of simple step, made of silica fused with an internal diameter of 5 and 300 mm in length, loaded with 0.5 g of catalyst, at atmospheric pressure. The reactant mixture was obtained from independent gases lines and controlled by mass flow controller, to obtain 1000 ppm of NO, 1000 ppm of CH₄ and 10% of O₂, using He as carrier gas. The resulting GHSV was set to 30,000 h⁻¹ based on the bed density of 0.5 g/cm³ for zeolites. The range of temperatures used was 300–600 °C. The reaction products were analyzed by gas chromatography, using a column of silica–alumina/Porapak Q of 2 m in length and a TC-mass detector.

2.3. Catalysts characterization

2.3.1. XRD and BET analysis

The catalyst were characterized by powder XRD patterns using a synchrotron radiation source in the Laboratorio Nacional do Luz Sincrotron, LNLS, Campinas, SP, Brazil. The reference XRD patterns of other possible phases in the materials were extracted from International Center for Diffraction Data. BET surface area determinations were carried out with an ASAP 2000 equipment.

2.3.2. Studies of NMR-MAS of ²⁷Al

The MAS ²⁷Al spectra were obtained at 27 °C recorded for all samples on a Bruker MSL 400 spectrometer. For ²⁷Al

(104.3 MHz), a 1.0 μs ($\theta = \pi/12$) pulse was used with a repetition time of 0.4 s. The chemical shifts are given in ppm versus [Al(H₂O)₆]³⁺ and 1 M Al(NO₃⁻) [33], for ²⁷Al NMR spectra.

2.3.3. Studies of temperature programmed ammonia desorption (TPAD)

Temperature programmed desorption data of ammonium for NH₄-BEA and NH₄-In-BEA were collected with an INSTR-ELEC programmer, which admits to change the heat slope during the run. The slope was 10–20 °C/min and a nitrogen flow of 10–20 ml/min was used. The desorbed products were analyzed using a FID detector.

2.3.4. Studies by Fourier transformed infrared spectroscopy (FTIR)

Infrared analysis of H-BEA and In-HBEA were performed on a JASCO 5300 spectrometer in the fingerprint region using KBr 0.05% wafer technique. Pyridine adsorption experiments were carried out using a thermostated cell with CaF₂ windows connected to a vacuum line, with a self-supported wafer adsorbed at 10⁻³ Torr and desorbed at 350–400 °C at 10⁻³ Torr for 4 h.

3. Results and discussion

3.1. XRD and BET

The surface area obtained by BET were 379 m²/g for H-BEA and 370, 369, 366 m²/g for samples A (IELP), B and C

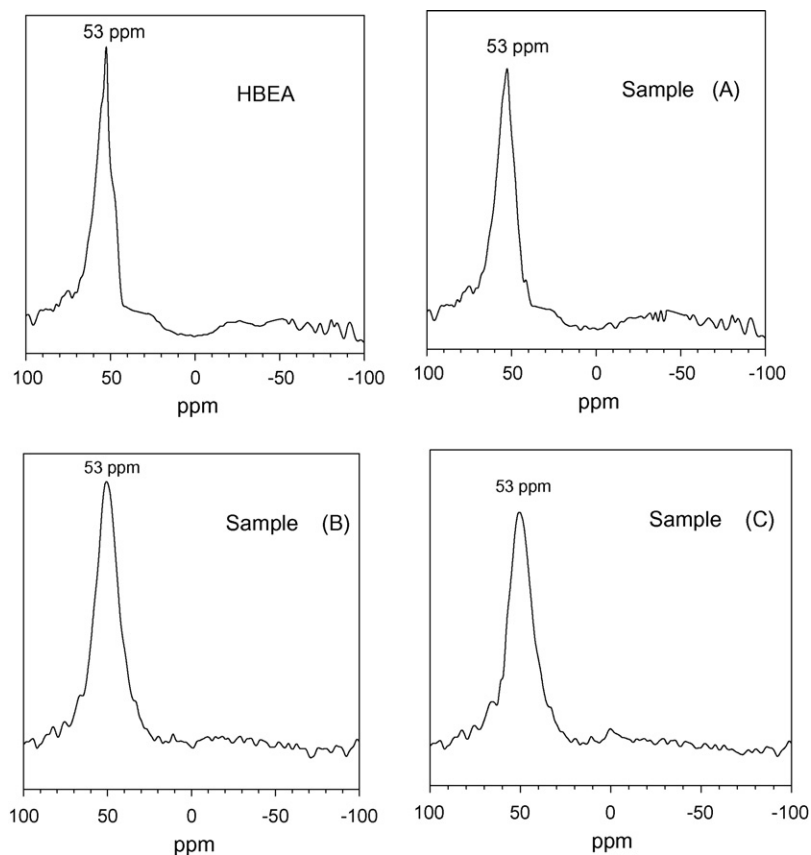


Fig. 2. ²⁷Al solid-state MAS NMR spectra of H-BEA and In-HBEA: samples A–C (see the text).

(IESP), respectively. X-ray diffraction analysis with synchrotron radiation confirms the tetragonal symmetry of the synthesized material, with the following lattice parameters: $a = b = 12.66$, $c = 26.41$ Å, framework density = 15.11 T/1000 Å³, free of others phases. Thus, XRD analysis show a crystallinity of 100% for H-BEA and >99% for samples A and B indicating that the In incorporation did not reduce either the surface area of the raw material used for its preparation nor the symmetry of its structure (see Fig. 1). In this figure we also show the signal of the diffraction pattern of In₂O₃ used in the preparation of the samples by ion exchange in liquid phase and in solid phase. The figure shows huge In₂O₃ crystalline phase in as made sample (IESP), but a highly dispersed In₂O₃ crystalline phase may be present (detected by PAC, see Part II), taking account that they are practically absent in XRD studies of the samples A and B.

3.2. NMR-MAS of ²⁷Al

Fig. 2 shows the ²⁷Al solid-state MAS-NMR spectra of HBEA and In-HBEA samples. The spectra exhibit two peaks with shifts of 53 ± 2 and 0 ± 2 ppm. The signal at 53 ± 2 ppm is assigned to tetrahedrally coordinated framework aluminium (*T_d*-Al). The signal at 0 ± 2 ppm is assigned to octahedral coordinated (*O_h*-Al) non-framework aluminium. As it can be observed, aluminium was incorporated mainly with tetrahedral coordination in the framework of H-BEA, prepared by the sol-gel procedure. The results obtained for samples A–C indicate that, the incorporation of indium does not introduce alteration in tetrahedrally coordinated framework aluminium (*T_d*-Al), except a little proportion of *O_h*-Al present in sample C. Thus, ²⁷Al NMR data of our samples suggest that the sol-gel method employed to synthesize HBEA zeolite, thermal-programmed post-synthesis treatment and the indium loading method, by IELP and IESP (sample B specially) are optimum to obtain In-HBEA zeolite with Al mainly in the tetrahedral framework position.

3.3. Temperature programmed desorption (TPD)

The analyses of TPD of ammonia from NH₄-BEA before and after the incorporation of In are shown in Fig. 3. The maximum speed of mass lost was reached at 325 and 278 °C for NH₄-BEA and NH₄-In-BEA (sample A), respectively. These results confirm that the incorporation of In was obtained by exchange with ammonium ions interacting with the zeolite framework at high temperature, and a low proportion of ammonium ions retained weakly by the zeolite has not been exchanged by Inⁿ⁺, in concordance with previous report using Zn²⁺ and Ga³⁺ [34], suggesting a possible back-exchange of the cation.

3.4. FTIR

Fig. 4a shows the spectra of the following samples: X-BEA (amorphous xerogel), Na-BEA and H-BEA and Fig. 4b, samples A–C. In the sample X-BEA the bands at 525 and 575 cm⁻¹ characteristic of BEA zeolite are absent, but they are present in the other samples. At the same time, the incorporation of In

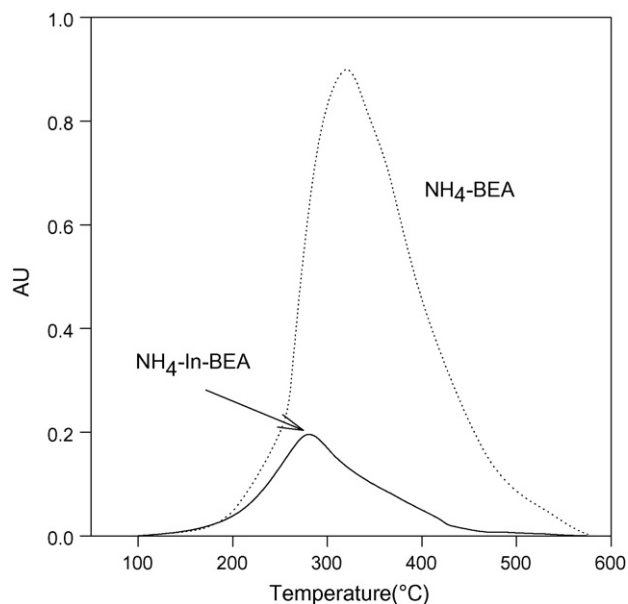


Fig. 3. TPD of ammonia from NH₄-BEA and NH₄-In-BEA (sample A).

does not modify the spectra. In all the samples, a broad band is observed at 952 cm⁻¹, indicating the tetrahedral aluminum presence. The band at 1104 cm⁻¹ observed by Chatterjee [35], indicating that it is representative of framework In(OSi)₄ in BEA as well as in MFI zeolite, does not appear in our samples.

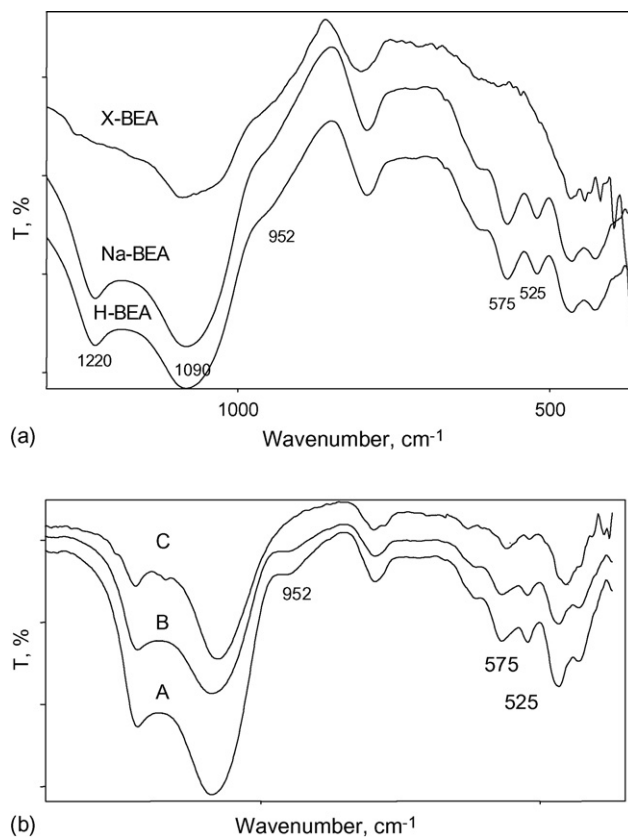


Fig. 4. (a) Infrared analysis of samples X-BEA (amorphous xerogel), Na-BEA and H-BEA in the fingerprint region. (b) Infrared analysis of samples A–C in the fingerprint region.

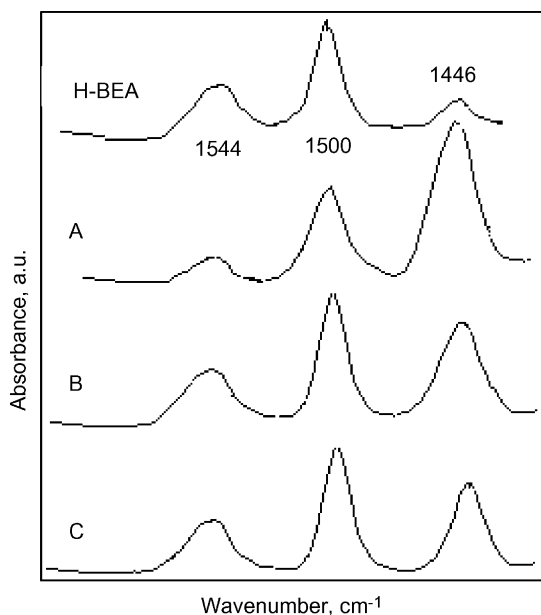


Fig. 5. FTIR spectra of pyridine adsorbed at room temperature and 10^{-3} Torr and desorbed at 400°C and 10^{-4} Torr during 4 h for H-BEA and In-HBEA: samples A–C.

Table 1

FTIR data of acid sites as a function of pyridine retained at 350 and above 400°C , respectively, on H-BEA and In-HBEA

Catalysts	Brønsted sites ^a		Lewis sites ^a	
	350 ^b	400 ^b	350 ^b	400 ^b
H-BEA	0.180	0.150	0.040	0.020
Sample A	0.032	0.014	0.170	0.140
Sample B	0.065	0.030	0.120	0.090
Sample C	0.100	0.080	0.090	0.070
Sample AM	0.180	0.150	0.040	0.020

^a FTIR, pyridine mmol/g retained at different temperatures before desorption at 10^{-4} Torr for 4 h.

^b Temperature [$^{\circ}\text{C}$] desorption of pyridine.

3.4.1. Pyridine adsorption studies

The results of FTIR in the OH^- stretching (Brønsted acid sites) absorption zone, and the absorption bands characteristics of pyridine, adsorbed and desorbed in vacuum at 350 and 400°C , allowed us to determine the effect of In species incorporated onto the samples. When the pyridine is eliminated at 350 and 400°C , the bands due to the strong OH^- sites are slightly recovered. Thus, following the absorption bands of pyridine at 1446 and 1544 cm^{-1} , attributed to pyridine adsorbed on Lewis acid sites and Brønsted acid sites, respectively, we determinate the quantities of these acid sites (Fig. 5 and Table 1). It is possi-

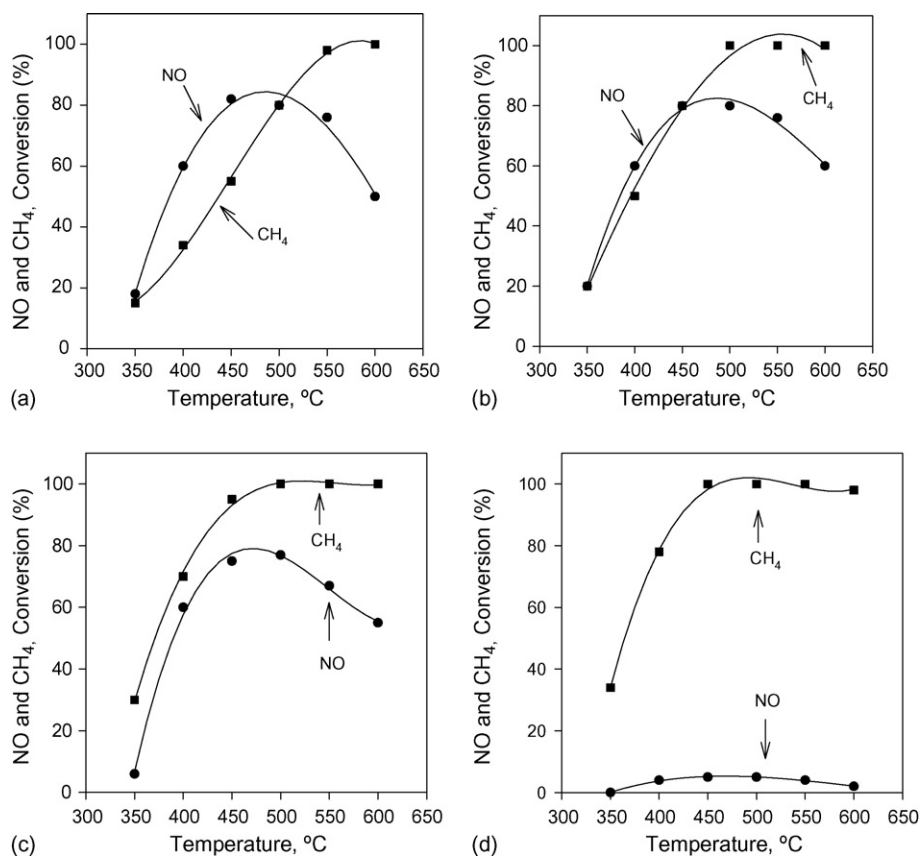


Fig. 6. Catalytic activity of In-HBEA at different temperatures for NO SCR. NO conversion to N_2 , and methane conversion for: (a) sample A: IELP activated in air at 500°C ; (b) sample B: IESP reduced at 500°C under H_2 and then oxidized at 500°C ; (c) sample C: IESP reduced under H_2 at 300°C and then oxidized in air at 500°C ; (d) sample AM: as made sample ($\text{In}_2\text{O}_3/\text{HBEA}$) without post treatments.

ble to suggest that the incorporation of In diminished the strong Brønsted acidity and increased the strong Lewis sites respect to those found on H-BEA zeolite. This is indicated in Table 1, expressed in mmol/g of pyridine retained at two temperatures for H-BEA and for the different samples of In-HBEA. According to the data shown in Table 1, the sample A has more strong Lewis sites than the others, but the proportion of Brønsted sites is: sample C > B > A. Two partially overlapping bands at 1446 and 1455 cm^{-1} (after pyridine adsorption), in the spectrum of H-BEA, generally observed in zeolites containing extra framework aluminum [36], was not found in our samples, indicating the effective method to incorporate Al in the framework using the sol–gel method.

3.5. Catalytic activity

In Fig. 6, the results of the catalytic activity for the selective reduction of NO with methane in the presence of oxygen are shown. As we can see, the conversion of NO reached approximately an 80% for samples A and B at 450 °C and the methane conversion was 55 and 80%, respectively (Fig. 6a and b). Fig. 6c shows the sample C activity, indicating a diminution of NO conversion at 500 °C with an increase of methane direct conversion to CO and CO₂ (reaching at 100%). Moreover, for the sample AM (Fig. 6d), the NO_x conversion is very low, but methane reached a conversion of 100%; this fact is in agreement with the higher amount of Brønsted sites and lower Lewis sites, compared with the other samples, showing that there is not any interaction between HBEA and In₂O₃ in this sample (see Table 1).

In-HBEA prepared by ion exchange in liquid phase using InCl₃ (sample A) and In-HBEA prepared by ion exchange in solid phase (sample B) are the most selective materials for the reduction of NO with methane; in this way methane is consumed selectively for the reduction of NO to N₂ at 450–500 °C, this fact can be observed especially in the case of sample A.

4. Conclusions

The BEA zeolite was obtained by means of a new and fast process of synthesis. This method reduces the aluminum as octahedral one (EFAL), diminishes the period of crystallization to 48–60 h, increases the percentage of crystallinity of the material and diminishes the content of the template agent reducing the costs. In incorporated on the zeolite does not modify its framework stability. The incorporation of In by ion exchange in liquid phase, diminishes the presence of ammonium cation as counter ion with the framework of the zeolite. The concentration of strong Brønsted acid sites decreases whereas the strong Lewis acid sites increases. A good correspondence between the catalytic activity and characterization of the materials was obtained. Pyridine retained for the zeolite at different temperature followed by FTIR indicated that new and strong Lewis acid sites in In-HBEA zeolites are formed in concordance with TPAD analysis.

The results obtained with In-HBEA prepared by ion exchange in liquid phase using InCl₃, and In-HBEA prepared by ion exchange in solid phase reduced at 500 °C and then oxidized

at 500 °C, orient us toward the supposition that these materials are more selective for the reduction of NO_x with methane than In-ZSM-5 [31]. Using these In-HBEA zeolites, methane is consumed selectively for the reduction of NO to N₂ at 450–500 °C, particularly for the sample obtained by ion exchange in liquid phase with InCl₃.

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