

ENVIRONMENTAL APPLICATION OF NATURAL MICROPOROUS ALUMINOSILICATES: NO_x REDUCTION BY PROPANE OVER MODIFIED CLINOPTILOLITE ZEOLITE

Botto, I.L.; Canafoglia M.E.

Centro de Química Inorgánica (CEQUINOR-CONICET), Facultad de Ciencias Exactas,
Universidad Nacional de La Plata, 47 y 115, La Plata (1900), Argentina.
FAX :+(54-221)4259485; E-mail: botto@quimica.unlp.edu.ar;

Lick, I.D.; Cabello, C.I.

Centro de Investigación y Desarrollo en Ciencias Aplicadas (CINDECA-CONICET),
Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 47 N° 257, La Plata
(1900), Argentina.

Schalamuk, I.B.

Instituto de Recursos Minerales (INREMI-CICPBA), Facultad de Ciencias Naturales y
Museo, 60 y 122, La Plata (1900), Argentina

Minelli, G.; Ferraris, G.

Istituto di Metodologia Inorganica e di Plasma (IMIP), Universidad "La Sapienza", Roma
(00185), Italia

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Dedicated to Prof. Pedro J. Aymonino on the occasion of his 75th birthday*

Abstract

Synthetic exchanged zeolites have proved to be active catalysts for the selective catalytic reduction (SCR) NO_x by hydrocarbons as reductors in the presence of O₂. The abundance and potentiality of argentine zeolite mineral resources encouraged us to analyze the possibility of taking advantage of these minerals as starting materials for catalyts preparation. In this sense, clinoptilolite-rich tuffaceous material was selected. Clinoptilolite (named CLI), belonging to the heulandite-type zeolite (HEU), was treated with Co(II) and Co(II)-Rh(III) solutions to obtain the monometallic and bimetallic zeolite systems, precursors of the catalysts. The mineral, the precursors and the catalysts were characterized by means of several techniques such as XRD, XRF, FTIR and DRS spectroscopies, thermal studies (DTGA, TPR), SEM-EDAX microscopy and textural analysis. The steps of the chemical treatment were carried out, in part, in solution, involving the mineral transformation into the NH₄-CLI, Co(II)-CLI and Co-Rh-CLI precursor phases. Catalysts were obtained by thermal treatment at 500°C. TPR measurements provided information about the interactions and characteristics of the active metals with the aluminosilicate framework of the catalysts.

Two types of catalysts were evaluated for the NO_x reduction reaction using propane in O_2 presence: 0.5%(w/w)Co-CLI and 0.25%(w/w)Rh—0.5%(w/w)Co-CLI respectively. The performance of catalysts obtained from natural zeolites revealed that they were active for the reaction, despite the very low metallic content.

Resumen

Las zeolitas sintéticas intercambiadas con metales han demostrado ser activos catalizadores para la reducción catalítica selectiva (SCR) de óxidos de nitrógeno (NO_x) mediante el uso de hidrocarburos como reductores, en presencia de O_2 . La abundancia y potencialidad de los recursos naturales argentinos en zeolitas, nos impulsó a analizar la posibilidad de aprovechamiento de esos minerales para su uso como materiales de partida en la preparación de catalizadores. En tal sentido, se seleccionó material tobáceo, rico en clinoptilolita. La clinoptilolita (denominada CLI) fue tratada con soluciones de Co(II) y de Co(II)-Rh(III) para obtener sistemas zeolíticos mono- y bimetalicos, precursores de los catalizadores. El mineral, los precursores y los catalizadores fueron caracterizados mediante distintas técnicas, tales como XRD, XRF, espectroscopías FTIR y de reflectancia difusa, estudios térmicos (DTGA, TPR), microscopía electrónica de barrido (SEM-EDAX) y análisis texturales. Las etapas del proceso químico fueron, en parte, en solución acuosa, implicando la transformación del mineral en las fases precursoras NH_4 -CLI, Co-CLI y Rh-Co-CLI. Los catalizadores fueron obtenidos por tratamiento térmico a 500°C. Las medidas de TPR permitieron obtener información acerca de la interacción y características del metal activo en el esqueleto aluminosilícico de los catalizadores. Se evaluaron dos tipos de catalizadores para la reacción de reducción de NO_x a N_2 mediante el empleo de propano, en presencia de O_2 : 0,5 % (en peso) Co-CLI y 0,25 % (en peso) Rh- 0,5 % Co-CLI. El comportamiento de los catalizadores obtenidos a partir de zeolita natural reveló que ellos son activos para la reacción, no obstante el muy bajo contenido metálico.

Introduction

Natural zeolites are aluminosilicates with a 3D framework, building from TO_4 tetrahedra (T=Al, Si), delimiting channels and cages of different dimensions. Molecular sizes of 6, 8, 10 and 12 member ring openings are ranged between 3 to 7.5 Å [1].

Zeolites can be distinguished from some other tectosilicates by the framework density (FD) expressed as number of T atoms per 1000 Å³ [1,2]. This parameter (ranged between 12 and 20 for zeolites and higher than 20 for non-zeolitic framework structures) is related to the pore volume but it does not reflect the size of the pore openings. Hence, the application of zeolites in adsorption and ion exchange processes is derived from this structural feature [2].

The second half of 20th century was transcendent in the zeolites development. From the geological point of view, enormous deposits of zeolite bearing rocks were discovered in many parts of the world. Likewise, the interest in inorganic ion exchangers was connected with the growth in the nuclear industry and the need of suitable ion exchangers for processing radionuclide-containing waters. The stimulated fundamental research on inorganic ion exchangers points out the selectivity and specificity for certain ions, opening the way for applications in the treatment of industrial exhausted solutions, in wastewater treatments and pollution control [3-5].

On the other hand, the synthesis of zeolite-analogues and the preparation of new materials from the bare mineral species have been topics of considerable interest. So, the exceptional physicochemical properties of these microporous materials offered new and interesting perspectives

for basic and applied studies in the chemistry field. Hence, at the present time, a wide range of applications in petrochemistry, fine chemistry, environmental protection, agronomy and more recently in the pharmaceutical industry and medicine are based on the functionalization of these materials [2,6-8]. In all cases, inorganic chemistry plays a crucial role in the scope of the zeolite development: not only in designing and discovering new zeolite-like materials, but also in the chemistry routes to transform natural species in useful compounds as well as in the study of structural, thermal and spectroscopic properties.

Although the natural microporous aluminosilicates were extensively used in environmental protection (waste managements) from processes related to ion-exchange in solution, the usefulness of zeolite tuffs in catalysis is limited and recent [9-12]. In this field the pioneering works were directed by the synthetic zeolites.

The increasing of toxic NO_x emissions from anthropogenic activities and the interest in improving the environmental control promoted the formulation of novel materials as active/selective catalysts for the nitrogen oxides reduction. In this sense, several synthetic exchanged Metal-zeolites (M= transition element) showed to be attractive catalytic materials for the selective catalytic reduction (SCR) of NO_x by hydrocarbons in oxygen presence [13,14].

The aim of this work is to study applications of argentine zeolitic tuffs taking into account the abundance, availability and low cost of these natural resources in our country. The structural, thermal and chemical characterization of natural zeolites was made with the purpose of using them in the preparation of monometallic (Co) and bimetallic (Co/Rh)-zeolite catalysts. The catalytic performance of these materials for the model reaction of NO_x - reduction to N_2 by means of propane (SCR) in presence of O_2 was evaluated. Clinoptilolite-rich tuff was selected for the transformation in catalytic materials. Bare and treated minerals by means of inorganic methods (ion-exchange precursors) were analyzed by SEM-EDAX microscopy, FTIR and DRS spectroscopical techniques, XRD analysis and thermal and textural methods. The catalytic performance of the NO_x -SCR reaction resulted from the comparison with the Co/ Al_2O_3 catalytic testing data providing supplementary evidence for the potentiality of mineral species in the preparation of useful materials.

Experimental

Samples of clinoptilolite from different deposits of our country were characterized by means of X-ray diffraction (XRD), atomic absorption spectroscopy and X-ray fluorescence analysis (XRF) (University of Geneve), SEM-EDAX microscopy and thermal (DTGA) and textural studies. The surface data were obtained by N_2 adsorption-desorption at 77 K using a Micromeritics ASAP 2010 analyzer. The samples were preheated under vacuum in two steps of 1h at 100°C and 1 h at 200°C. BET specific surface area, were obtained from adsorption data in the relative pressure range 0.05-0.2. BJH pore size distribution [15], were obtained from data of the desorption branch of the isotherm micropore analysis by *t*-test [16], adopting the Harkins & Jura reference curve [17] and total pore volume by Gurvitsch rule [18]. Original sample showed a specific area of $\sim 10 \text{ m}^2/\text{g}$ whereas the specific areas of exchanged samples were between 11 and $14 \text{ m}^2/\text{g}$, depending on the treatment.

The thermal stability was also analyzed by means of “in situ” XRD analysis (in air and in water vapour atmospheres) up to $\sim 700^\circ\text{C}$.

From the preliminary study, a clinoptilolite-rich sample with the chemical composition given in table 1 was selected to use as parent tuffaceous material in the preparation of the precursor phases leading to the catalysts by thermal activation. A small proportion of SiO₂ (quartz form) was observed in all samples as a subordinated mineral. The presence of vitreous phase (rhyolitic glass) was observed by petrographical microscopy. Volcaniclastic material is the precursor of sedimentary zeolite from reaction in an open hydrological system. From the geochemical point of view, the general hydration sequence: Glass + H₂O → clinoptilolite + ions, left a small proportion of SiO₂ that crystalized as a late alteration product.

Table 1: Chemical analysis of bare clinoptilolite by XRF analysis
Majority elements (as % oxides)

SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	H ₂ O
66.99	0.16	13.39	0.87	0.00	0.01	0.99	2.54	3.53	1.48	0.04	10.08

Minority elements (in ppm)

Nb	Zr	Y	Sr	U	Rb	Th	Pb	Ga	Zn	Cu	Ni
25	79	28	1421	<2	37	10	10	11	22	13	<2
Co	Cr	V	Ce	Nd	Ba	La	S	Hf	Sc	As	
<2	9	16	43	16	381	21	5768	6	7	<3	

Although clinoptilolite is characterized by a K>Na content, the studied sample showed an inverse trend, which can be explained by the zeolite genesis from the hydrolysis of the volcaniclastic material in a Na-rich saline solution.

In a first step, CLI was treated with ammonium chloride solution to exchange alkali and alkaline-earth elements by NH₄⁺. Treatments were done at different experimental conditions: i) from RT up to 120°C, ii) from 24 to 240 h., iii) at different ammonium concentration iv) with and without stirring. These preliminary treatments permitted to select the conditions to obtain NH₄-CLI. So, 10g of (Na,K)CLI were treated with excess of NH₄Cl 0.5 M at RT for 24 h. with constant stirring. The sample was heated up to 300°C for 24 h to eliminate partially the NH₄⁺. The complete evolution of NH₃ occurred at ~500°C to give the acid zeolite, (named H-CLI).

The monometallic Co-CLI precursor of catalysts was obtained by treating NH₄-CLI with cobalt acetate solutions (variable concentration). Selected conditions to obtain Co-CLI were as follows: 5 g of NH₄-CLI (after thermal treatment at 300°C) were treated with solution of cobalt acetate 0.01 M at RT for 12h (with stirring). The profile of the ion exchange isotherm in the experimental conditions led to a 0.5% (w/w) Co. The isotherm reports the equivalent fraction of the incoming cation, present at equilibrium in the liquid phase vs the equivalent fraction of the cation in the zeolite. The chemical analysis of cobalt was made by AAS considering the initial and final concentration of the cobalt acetate solution used in the treatment. Standards of cobalt acetate were used.

The bimetallic Rh-Co-CLI precursor was obtained from treating 2 g of Co/CLI (0.5 % Co) with a Rh(III) chloride solution (10^{-4} M) until dryness (final content of Rh = 0.25% (w/w)).

The catalysts were obtained from the precursors by treatment at 500°C in flowing air for 3 h.

FTIR spectroscopy was particularly used to analyze the NH_4 exchanging and its elimination by heating. Measurements were carried out in a Bruker (IFS-66) Spectrophotometer with the KBr pellet technique.

The DRS spectra were registered in a Beckman DK1 spectrophotometer between 2500 and 210 nm, by using MgO as reference.

DTGA were registered on a Shimadzu 50 equipment under inert atmosphere.

Thermal studies in a reducing atmosphere ($\text{H}_2/\text{N}_2=10/90$) were made in a home-made temperature programmed reduction equipment (TPR). This technique enables the determination of interactions of the cobalt species with the zeolitic framework.

Catalytic reactions were evaluated in a fixed bed reactor, heated electrically and the temperature measured by means of a thermocouple of the K type in contact with the catalytic bed. The reaction mixture was obtained from four feed lines: NO-He, methane or propane /He, O_2 /He and He as balance. Before reaction the catalysts were activated at 500°C for 1 h.. The reaction was carried out between 250 and 700°C. The reactant mixture had a composition 1500ppm of NO, variable concentration of O_2 (0.8-2.5 %), 2000ppm of C_3H_8 and space velocity (GHSV) of 8600 h^{-1} . The catalyst mass used was 0.400 g and the total flow rate was 50 ml/min. Reaction products were analyzed by using a gas chromatograph, Shimadzu GC-8a, provided with a thermal conductivity detector. The separation of products was performed with a concentric column CTRI (Altech).

Catalytic NO- N_2 conversion is calculated as $X_{\text{N}_2} = 2[\text{N}_2]/[\text{NO}]$ whereas the propane conversion (to give CO_2), as the secondary reaction of combustion, is expressed as $X_{\text{CO}_2} = 1/3 [\text{CO}_2]/[\text{C}_3\text{H}_8]$.

Results And Discussion

Clinoptilolite (CLI) is a sedimentary zeolite with a typical chemical composition $(\text{Na,K})_6(\text{Al}_6\text{Si}_{30}\text{O}_{72}) \cdot 20\text{H}_2\text{O}$. This is the most abundant of natural zeolites and can be classified as a silica-rich member ((Si/Al) ratio ~5 and FD=17). The framework topology is characterized by a two dimensional pore system with the presence of 8-ring channels that intersect two parallel 10-ring and 8-ring channels respectively ($[100] \ 8.2.6 \times 4.7 \text{ \AA} \rightarrow \{[001] \ 10.3.0 \times 7.6 + 8.3.3 \times 4.6\}$) [2,19]. This zeolite presents good adsorption properties for CO_2 , SO_2 , NH_3 and NO_x gases [2]. The relatively open structure of heulandite-type zeolites enhances the sorption properties. The chemical composition of the aluminosilicate framework, modulates the ion exchange property. This is expressed as cation exchange capacity (CEC) and it can theoretically reach 330 meq/100g [20].

CLI is highly selective for the ammonium cation. The selectivity sequence at RT is $\text{NH}_4 \sim \text{K} > \text{Na} > \text{Ca} > \text{Mg}$. According to these data, it is expected a low incorporation of Co. However, this is much more effective when the CLI was previously exchanged with NH_4 . The NH_4 exchange is

an indirect method to obtain the H-CLI that avoids the use of an acid treatment. Likewise, the protonic acid site seems to play a synergistic role interacting with the metallic specie in the metal modified synthetic zeolite catalysts [9].

There are different sorption mechanisms including the so-called ion exchange. The sorption of metallic ions seems to be affected by a combination of factors, corresponding to the physicochemical characteristics of both, the solution and the solid. Ion exchange depends on the temperature, the pH and concentration of the solution and particularly on the hydrated ionic radii of the ions as correlated to the zeolitic channels. The temperature enhances the ion exchange while the pH is also critical [21]. So, the most optimum conditions for successful metal loading should be related to exchange cations of low valence and large size (small hydrated radius) by using increased temperature and rather high pH (in order to minimize the effect of mobile H^+ ions). The high specific surface area as well as the long treatment time (by a stepwise process) favour the ion exchange [21]. In HEU-type zeolites the ion exchange is easy for alkali and alkaline earth elements but it is not so clear for transition ion elements. In this case, the process is strongly dependent on the aqueous chemistry of the "d" species and thus the hydrolysis reactions can give soluble and/or insoluble products that interact with the microporous zeolite. As a consequence, the sorption mechanisms do not only comprise the ion exchange process (absorption into the channels in the aluminosilicate framework) also adsorption (specific and/or non-specific regarding inner-sphere and/or outer-sphere surface complexation) and surface precipitation and coprecipitation processes. This last reactions can generate non-stoichiometric phases, composite materials, metal ions supported on the surface, etc) [22,23].

The synthesis of HEU-type zeolites modified by Co was reported in the literature [21], although controversial opinions were expressed respect to the Co-content. The highest reported value was 7.5%(w/w). With this concentration the simultaneous presence of Co species as supported phases, segregated oxides and exchanged zeolite were suggested by SEM-EDAX as well as XPS results [21]. The presence of Co(III) in the form of composite materials or segregated phases are strongly dependent on the Co loading. Another information about Co-HEU type zeolites was available by Kim et al. [24]. They reported the synthesis of a exchanged Co-CLI zeolite with the $Co_{1.9}H_{1.5}Al_{5.3}Si_{30.7}O_{72}$ composition (Si/Al \sim 5.8) [24]. However even at the highest surface area of synthetic zeolite (114 m^2/g) and under drastic experimental conditions, the full exchange by cobalt was not reached. The reported exchange corresponds to a cobalt content of \sim 5 % (w/w) [24].

It is common that natural zeolites present a very low surface area. This characteristic can be particularly attributed to a pore blockage of the crystalline zeolite phase by the vitreous zeolite-precursor. Because of a great affinity for the ammonia ion, it is possible to get, by ion exchange, the monoionic ammonia form of CLI. Thus, we have observed by EDAX that all ions, except a part of potassium were exchanged by NH_4 . However, a mild conditions employed for the Co exchange (RT) led to the very low content of this metal (only 0.5 % (w/w)).

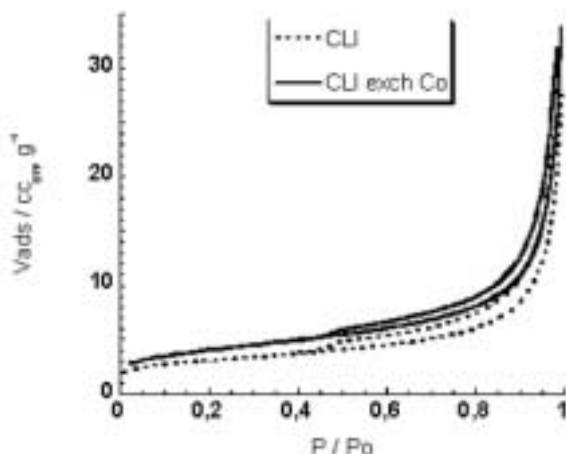


Figure 1: Nitrogen adsorption-desorption isotherms at 77 K for Clinoptinolite (CLI) and Co-containing Clinoptinolite (Co-CLI)

Fig 1 shows the nitrogen adsorption-desorption isotherms at 77 K for CLI and Co-CLI respectively. In order to evaluate the total pore volume, the Gurvitsch rule has been applied to the adsorption data at $P/P_o = 0.99$ (instead of the usual value of $P/P_o = 0.95$ adopted when a definite plateau is present). The hysteresis loop of the desorption branch reveals the existence of large pores (meso and macroporous) and a limited amount of micropores in the samples. It is evident that the two samples do not possess the typical porous structure expected for synthetic zeolites as silicalite and ZSM-5, which give rise to another type of adsorption isotherms according to the classification of Brunauer, Deming, Deming and Teller (BDDT) [25].

Results given in Table 2 indicate that the preparation method to introduce cobalt does not significantly modify the textural parameters of the host structure. However, it is known that an increase of micropore and external/macropore area is clearly observed after ion exchange of natural HEU with ammonium [9]. That is, the preparative method for the incorporation of Cobalt restored part of the original mesoporosity of the host matrix.

Table 2. Textural features of CLI and Co-CLI precursor

SAMPLES	BET area $m^2 g^{-1}$	V_{tot} ML g $^{-1}$	S_{ext} $m^2 g^{-1}$	$V_{1/4}$ mL g $^{-1}$	$D_p \text{Å}$
CLI	11.0	0.043	8.4	0.001	n.d.
Co-CLI	14.5	0.052	11.8	0.001	n.d.

The DTGA plots of CLI, NH_4 -CLI and Co-CLI, shown in Fig 2, reveal the water loss up to $\sim 250^\circ C$.

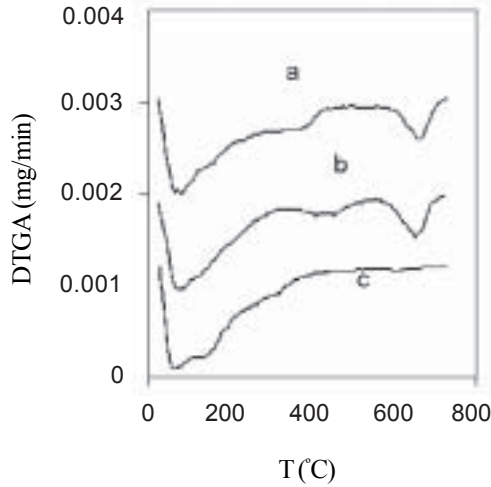
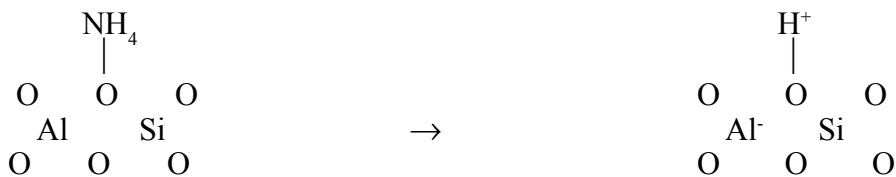


Figure 2: DTGA plots of: a) $\text{NH}_4\text{-CLI}$, b) Co-CLI , c) CLI

The NH_3 loss from the $\text{NH}_4\text{-CLI}$ (curve a) is observed at $\sim 380^\circ\text{C}$, a situation that leads to the formation of Brönsted acid sites (H-CLI). The Co-CLI (curve b) obtained from $\text{NH}_4\text{-CLI}$ partially transformed in the acid form at 300°C , clearly reveals the presence of NH_4 ions. In this case the NH_3 evolution occurs at higher temperature than that observed for the $\text{NH}_4\text{-CLI}$ (420°C). The temperature shifting can be attributed to the selective adsorption of this gas as well as the interaction between Co(II) and NH_3 . This is not unexpected because the intrazeolitic or surface cobalt ions are Lewis acid centres that can retain easily the NH_3 Lewis base.

Figure 3 shows the FTIR spectra of $\text{NH}_4\text{-CLI}$. The splitting of the NH_4 bending-mode ($\sim 1400\text{ cm}^{-1}$) is attributed to the lowering of the T_d symmetry by interaction with the aluminosilicate framework. A higher intensity of the band at 1640 cm^{-1} (in comparison with the band of water of the untreated CLI), corresponds to the overlapping of the bending mode of water with some component of the NH_4 splitting. The presence of adducts between the ion and the acid sites of the zeolite can be suggested [26].

The interaction between the zeolite framework and NH_4 ions and the further alteration by heating can be drawn as:



although the formation of $\begin{array}{c} \text{O} \quad \text{HO} \quad \text{O} \\ | \quad | \quad | \\ \text{Al} \quad \text{Si} \\ | \quad | \quad | \\ \text{O} \quad \text{O} \quad \text{O} \end{array}$ entities is also possible.

Finally, the presence of $\begin{array}{c} \text{O} \quad \text{O} \quad \text{O} \\ | \quad | \quad | \\ \text{Al}^- \quad \text{Si} \\ | \quad | \quad | \\ \text{O} \quad \text{O} \quad \text{O} \end{array}$ and $\begin{array}{c} \text{O} \quad \text{O} \\ | \quad | \\ \text{Al} \quad \text{Si}^+ \\ | \quad | \quad | \\ \text{O} \quad \text{O} \quad \text{O} \end{array}$

species can be observed at temperatures higher than 650°C [2].

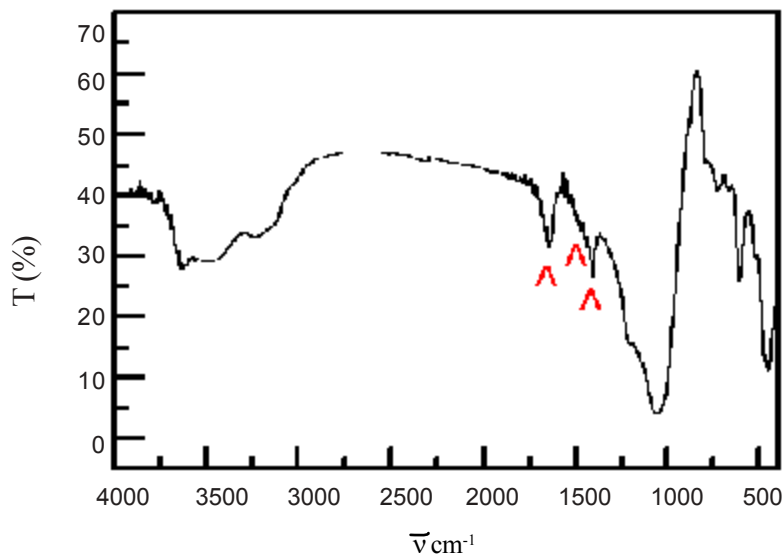


Figure 3: FTIR spectrum of $\text{NH}_4\text{-CLI}$ (between 4000 and 450 cm^{-1})

X-ray diffraction lines of the parent CLI remained intact during the NH_4 or Co(II) ion exchange, revealing the low effect of the extra-framework ions. Likewise, the structure of Co-CLI was preserved by heating up to $\sim 700^\circ\text{C}$. Fig. 4 shows the Co-CLI “in situ” X-ray diffraction pattern by heating up to 800°C .

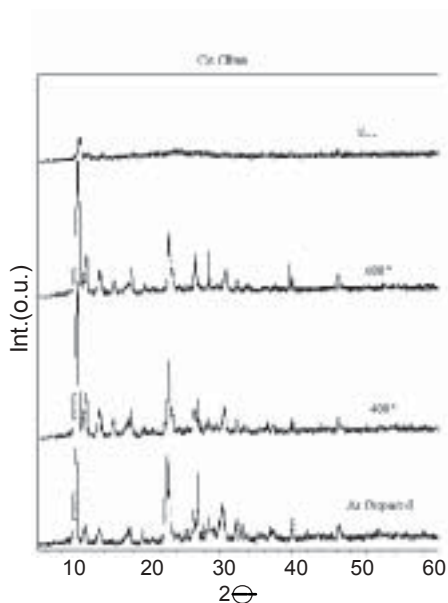


Figure 4: (in situ) XRD patterns of CoCLI (air atmosphere)

It is interesting to note that the thermal treatment is useful to differentiate clinoptilolite from heulandite [2]. Although heulandite and clinoptilolite are isotypic, the different stability can be related to the lower Si/Al ratio of the former. This is reliable for a different distribution of the

extraframework cations and consequently heulandite show a complete structural collapse at $\sim 450^\circ\text{C}$ [27]. The identity of the zeolite and the thermal stability of exchanged clinoptilolite was so corroborated.

The thermal behaviour in water vapour atmosphere is shown in Fig 5. The crystal structure remains without changes and only a slight loss of crystallinity is observed by heating up to $\sim 700^\circ\text{C}$. No clear signal of dealumination was registered by EDAX analysis.

Fig 6 shows the DRS spectra of Co-CLI precursor heated at 300°C . Although the Co content is low, weak signals of Co- d-d transitions are observed. The two broad bands in the 700 and 1400 nm seem to be related to the presence of Co(II) and Co(III) species, whereas the band at ~ 410 nm can be attributed to Co(III)-Co(II) CT [28]. In this sense, a re-arrangement of the original site of cobalt (associated to O atoms and water molecules) is observed by heating. The elimination of water suggests a lowering of local

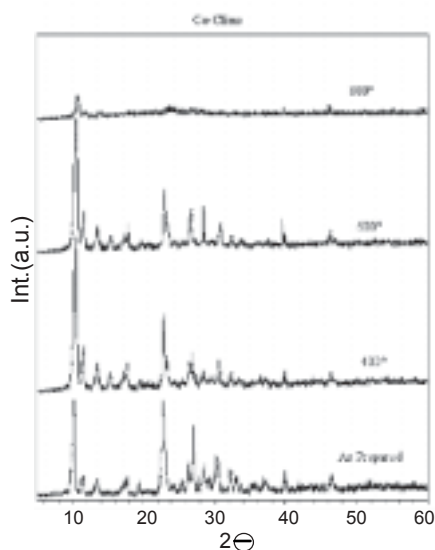


Figure 5: (in situ) XRD patterns of CoCLI (water vapour atmosphere)

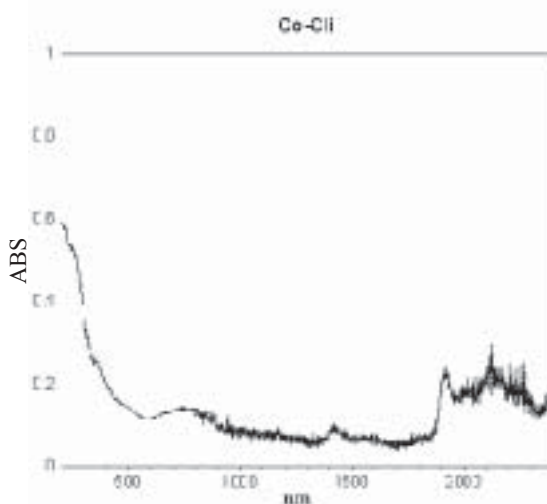


Figure 6: DRS of Co-CLI precursor (heated at 300°C)

symmetry of the metal site. A strong interaction effect is governed by the Co redox chemistry and by diffusional aspects. So, the redox properties and the metal site-symmetry are factors used to explain the efficient enzymatic catalysis through the pre-formation of a transition state so called “entatic state” [29]. It is expected that the redox chemistry of Co(II)-Co(III) is energetically favoured by a d^7 Co(II) distorted tetrahedral environment (with completely filled bonding e_g orbitals) and by d^6 low spin Co(III) in octahedral coordination (with the completely filled bonding t_{2g} orbitals). These facts, as well as the low content of Co in the precursor and the chemistry of this element in solid state decrease, still more, the resolution of the DRS spectrum of catalysts (500°C). So, the TPR technique, described below, will help to analyze the possible Co-interaction and/or segregation from the aluminosilicate framework.

It is evident that the zeolite framework (in the presence or absence of water) functions as a huge ligand to coordinate and stabilize the metal cations. The nature and extent of interactions

between the cations and zeolite framework, depending on the size and shape of the pores where the metals can be located, are useful to analyze the catalytic properties for the SCR reaction of NO_x by hydrocarbons. In general, it was suggested that the Co(II) sites in 8-ring channels are thermodynamically more stable than those in 10-ring channels for this reaction and consequently the CLI, with two types of 8-ring channels may play an important role in achieving the activity for NO_x reduction by CH₄ [24]. On the other hand, the migration of Co(II) ions to the internal sites of zeolite by temperature effect can be considered in the activation of the precursor to give the catalysts, without causing diffusional problems with the reactive molecules [24].

It is generally accepted that the reduction of NO_x by hydrocarbons in oxygen excess proceeds through a series of steps. So it is expected that adequate combination of metal species (redox properties) may give more active catalysts. In this sense, bifunctional catalysts containing transition metals of the first series "d" and some element of the Pt group may improve the catalytic activity and the tolerance of water vapour, preventing severe dealumination process after hydrothermal aging. Hence, the acid-base, redox and structural properties are related to the potentiality of H-Zeol, the synergetic effect and the topology of the aluminosilicate matrix toward the geometry and characteristics of reductor hydrocarbon. In this way, we direct the attention to the Rh-Co-CLI system. The presence of Rh does not affect the structural feature of clinoptilolite, according to XRD analysis.

An adequate form to analyze the interaction of metals with the aluminosilicate framework seems to be the temperature programmed technique (TPR). This method allows to identify the presence of segregated phases, intrazeolitic metal cations as well as metal ions supported on the surface. It is possible to know about the activation of the catalyst from the availability of metals for their reduction by H₂ [30]. The thermal behaviour under reduction conditions is observed in Fig. 7. The TPR pattern of zeolite parent clinoptilolite does not show signals of reducible species up to 950°C. In this sense, it is interesting to denote that only one weak signal of reduction appears at 980°C. This is subsequent to the aluminosilicate framework collapse, which left available iron species. This fact is very interesting because the TPR technique is revealed as a useful technique to show the existence of structural Fe(III) (by isomorphous replacement of Al(III)). In this sense, we are analyzing the reducing behaviour of different natural aluminosilicates (clays and zeolites), in which it is usual the presence of two types of iron species, according to the mineral genesis: those species related to the associated minerals as impurities (amorphous or crystalline Fe(III)-oxide-hydroxide such as goethite, limonite, haematite, etc) and the structural Fe(III), in the covalent framework.

The TPR pattern of the Co-CLI catalyst is characterized by two signals: the first one at ~580°C and the second one at ~900°C. This last shows a higher intensity than that observed in the bare CLI pattern and also appears at lower temperature. It is well known that binary cobalt oxides (CoO and Co₃O₄) as bulk present TPR signals in the 400 °C region, corresponding to the Co(III)-Co(II) and Co(II)-Co reduction processes [30]. The reducibility of cobalt species decreases when it is supported [30]. From the different Co-species in activated Co-Zeol systems the reduction temperature of extraframework cobalt (including free oxides and surface cations) is lower than that of intrazeolitic type. It can be established the following order: free Co-oxides (~400°C), surface cobalt (500-600°C) intrazeolitic and deeply anchored cobalt (temperature higher than 700°C) [31].

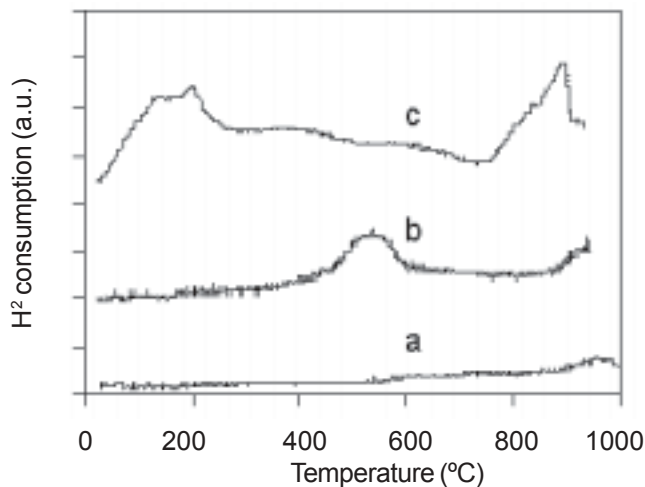


Figure 7: TPR patterns of : a) CLI, b) Co-CLI, c) Rh-Co-CLI

Hence, it can be clearly observed the presence of Co(II) and Co(III) of intermediate interaction and Co(II) species with a strong interaction but it can be disregarded the presence of free binary Co-O oxides (from segregated crystalline oxides or amorphous composites). These phases have been observed in related systems by heating the precursors at temperature higher than 650°C [30,32].

The incorporation of Rh(III) affects the Co(II) reducibility. Free Rh(III) oxide reduces at very low temperature (~135°C), according to experimental conditions [30]. It is also known that the reducibility of this metal can be affected in a supported system. Rh(III) supported on SiO₂ or TiO₂ reduces at lower temperature whereas when it is supported on more basic oxides, the reduction temperature is increased up to 250°C [30]. Therefore, we are in conditions to analyze the TPR pattern of the bimetallic catalyst Co(0.5%)-Rh(0.25%)-CLI. The first reduction zone, located between 50 and 300°C, can be associated to the Rh(III)–Rh process. From this reaction, the H₂→2H activation favours the intrazeolitic/surface Co(II) reduction, showing differences with the monometallic system. A continuous reduction process between 300 and ~650°C can be assigned to Co(II) species of different interaction. Likewise, the strong and asymmetric signal between 780 and 900°C is attributed to the Rh activation effect on the reducibility of Co(II) in the oxide matrix after the zeolite collapse and also on that of the structural iron.

Fig 7 gives the NO-N₂ conversion for the Co-CLI and Rh-Co-CLI catalysts measured as a function of reaction temperature at a GHSV of 8600 h⁻¹, according to the experimental conditions. Although the bare clinoptilolite (activated at 500°C) is slightly active for the studied reaction (conversion of 17% at 600°C), the Co-CLI catalyst shows an activity increase by metallic effect (maximum of conversion close to 31 % at 600 °C). The Rh-Co-CLI catalyst does not involve an increase of the activity (conversion of 40 %) but the reaction occurs at lower temperature (400°C).

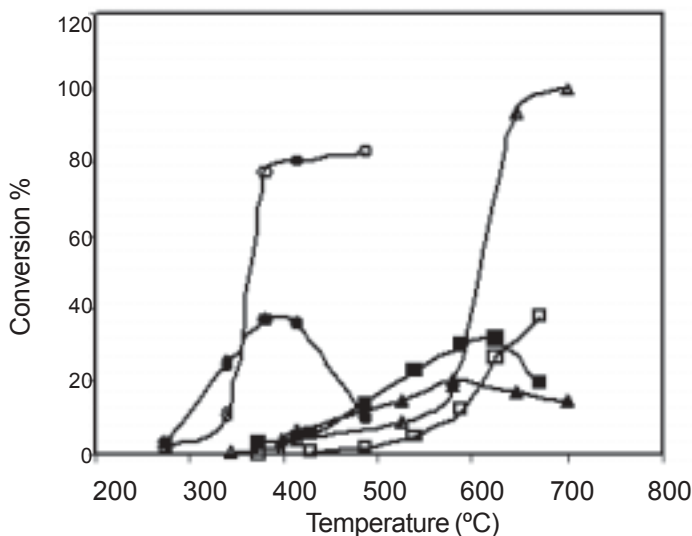


Figure 8: $NO-N_2$ conversion of CLI (\blacktriangle), Co-CLI (\blacksquare) and Rh-Co-CLI (\bullet). Corresponding data for the $C_3H_8-CO_2$ conversion are indicated by empty symbols.

Table 3 sums up data of $NO-N_2$ and of propane- CO_2 conversions by using the prepared Co-CLI and Rh-Co-CLI catalysts. Catalytic data of the $Co(1.5\%)/Al_2O_3$ reference system, previously treated at $1000\text{ }^\circ\text{C}$ (in similar experimental testing conditions[33]) and those of natural CLI activated at $500\text{ }^\circ\text{C}$ are included as reference. The propane- CO_2 reaction is associated to the total process where the hydrocarbon reduces the NO but also reacts with O_2 as a secondary process, delimiting the selectivity of the catalysts. In this sense, the catalyst promoted with Rh favours the secondary reaction to the detriment of the primary process. Thus, the diminution of the activity for the $NO-N_2$ reaction by the use of bimetallic catalyst is attributed to the competency between the primary and secondary reactions. The selectivity is thus very low for the assayed NO_x reduction process.

Table 3: Catalytic performance of studied catalysts (as conversion %) for $NO-N_2$ reduction (principal reaction) and $C_3H_8-CO_2$ oxidation (secondary reaction). Data of $Co(1.5\%)/Al_2O_3$ catalyst and activated CLI, in similar testing conditions, are included for comparison

Conversion reaction	$Co(1.5\%)/Al_2O_3$ $T_{max} = 650^\circ\text{C}$	$Co0.5\%CLI$ $T_{max} = 620^\circ\text{C}$	Activated-CLI at 500°C $T_{max} = 650^\circ\text{C}$	Rh-Co-CLI $T_{max} = 400\text{ }^\circ\text{C}$
$NO-N_2$	60	35	17	40
Propane- CO_2	23	30	100	82

Conclusions

On the basis of structural, thermal and spectroscopic properties, the studied mineral is a good raw material to be used in catalysis. However, it is possible to improve the performance of these alternative catalytic materials, profiting more adequately the mineral clinoptilolite as starting material. The Co-CLI catalyst shows good activity, in spite of the very low metallic content.

Likewise, an appreciable decrease of the reaction temperature is observed by using the Rh-Co-CLI catalyst, although the activity is similar to that of a monometallic system. These results are promising for the studied process and open up new perspectives for the industrial application of natural zeolites.

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