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NATURAL MATERIALS MODIFIED WITH TRANSITION METALS

OF THE COBALT GROUP: FEASIBILITY IN CATALYSIS

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Abstract

The chemical modification of a clinoptilolite-mordenite natural zeolite mixture (in a ratio close to 1) from an Argentinean deposit was done by means of different treatments. The procedure started with the exchange with ammonium and further heating at 400ºC to form an acid-zeolite mixture (indirect method). The treatment with Co(II) and Rh(III) aqueous solutions (by soft chemical process) led to modified zeolites containing 0.38 % Co(II) and 0.25 % Rh(III). These materials heated at 500ºC were proved as catalysts in the NO Selective Catalytic Reduction (SCR) process using propane as reducing gas. Physico-chemical characterization by different analytical techniques and the catalytic activity tests for the mentioned reaction were interesting to point out the technological potentiality of abundant and low cost natural species under inorganic treatments.

Key words: natural zeolites, chemical modification, catalysis, NO SCR process.

Resumen

Se ha procedido a la modificación química de una mezcla zeolítica natural procedente de un depósito argentino constituida por clinoptilolita y mordenita (relación próxima a 1). El tratamiento comprendió diferentes etapas que se iniciaron con la formación de zeolita parcialmente ácida, obtenida por el método indirecto de intercambio con amonio y calcinación a 400ºC. El posterior tratamiento con soluciones diluidas de sales de Co(II) y/o de Rh(III) (en condiciones suaves) permitió la caracterización de especies conteniendo 0.38 % de Co(II) y 0.25 % de Rh(III). Los geomateriales, tratados térmicamente a 500ºC fueron probados como catalizadores en la reacción de reducción catalítica selectiva (RCS) de NO a N_2 utilizando propano como reductor. La caracterización fisicoquímica por diferentes técnicas de la muestra original y de las modificadas así como la determinación de la actividad catalítica para la reacción indicada, permitieron puntualizar la potencialidad tecnológica de éstas especies minerales abundantes y de bajo costo, sometidas a tratamientos inorgánicos.

Palabras claves: zeolitas naturales, modificación química, catálisis, RCS de NO a N_2.

Introduction

A great number of synthetic zeolites exchanged by transition metals are applied in catalysis and particularly in the environmental NO selective catalytic reduction (SCR) process [1-10]. Mineral resources rich in zeolites are not commonly employed with this industrial purpose. However, these low cost and abundant materials are the most important inorganic cation exchangers in Nature.

According to the 3D open structural and chemical features, natural zeolites show high cation exchange sensibility, good adsorption and resistance to the temperature and excellent compatibility with the environment, facilitating the metal incorporation in the lattice, process that can affect the redox and acid-basic properties. All these possibilities are interesting to increase the potentiality of these systems in the catalysis field.

In our country the distribution of zeolite deposits is very extensive and predominantly they have a sedimentary origin. This fact ensures the adequate structural homogeneity and mineralogical composition, becoming these materials useful to catalytic applications.

The studied zeolitized rocks proceed from a deposit located close Telsen, Chubut, Argentina, where the material is basically a mixture of two of the more widely distributed zeolites in Nature: clinoptilolite and mordenite. Clinoptilolite presents a system of interconnected channels with 10 and 8 members respectively [11,12]. Mordenite presents two types of interconnected channels with 8 and 12 members, but the location of a third 8-membered channel block the diffusion in a highly puckered aperture [12].

This study aims to survey some aspects of the metal-lattice interaction by means of soft chemical treatment with diluted solutions of ammonium, cobalt and rhodium at room temperature, in order to analyze the catalytic performance of the modified natural system in the NO SCR reaction by propane. Different analytical techniques are used for the characterization of the original and modified phases.

Experimental

Zeolite tuff from an Argentinean deposit located in Telsen (Chubut, Argentina) was characterized by different techniques and chemically modified by using soft chemical treatments. So, the original mineral sample, mixture of clinoptilolite (or CLI) and mordenite (or MOR) as well

as the derivative geo-materials were characterized by XRPD, SEM-EDS, AAS, ICP-AES, FTIR, BET and TGA-DTG and TPR thermal studies.

Samples used in the NO SCR process were obtained from successive chemical treatments in aqueous solutions. The first step was the exchange reaction to form the ammonium phases. So, 10 g of zeolitized tuff were treated with NH_4Cl 0.5 M solution in excess at RT for 8 h with an initial stirring of 2 h. The modified zeolite was then heated at 400ºC (24 h) to give a partial acidic zeolite mixture. Catalytic precursors were prepared by treatment with diluted Co(II) acetate and Rh(III) chloride aqueous solutions as follows:

Assay I: 5 g of the acid zeolite mixture were treated with 20 ml of $Co(Ac)_2$ 0.01M for 12 h.

Assay II 1 g of acid zeolite mixture was treated with the necessary amount of a $RhCl_3$ (10^{-4} M) solution to obtain a Rh content of 0.25% w/w by dryness treatment

Assay III 1 g of material resulting of assay I was treated with a 10^{-4} M solution of $RhCl_3$ until dryness to obtain a Rh content of 0.25% w/w.

All samples were washed with water and heated at 80ºC for 24 h. The materials from assays I, II and III were identified as Co-CLIMOR, Rh-CLIMOR and Rh-Co-CLIMOR. They were finally thermally treated at 500ºC for 2 h to use as catalyst for the SCR reaction.

Catalytic reactions were evaluated in a flow fixed bed reactor electrically heated (CINDECA-CONICET La Plata-UNLP) [10]. The reaction mixture was obtained from four feed lines individually controlled: NO/He, C_3H_8/He, O_2/He and He to close the balance at 1 bar. The feed was constituted by 1500 ppm of NO, 2000 ppm of C_3H_8 and 2.5% of O_2. The total flow rate was 50 ml/min, the catalyst mass was 0.400g.

Reaction products were monitored with a gas chromatograph Shimadzu model GC-8A provided with a TCD detector. The separation of products was performed with a concentric column CTRI of Altech. This system permits the identification and quantification of O_2, N_2, N_2O, CO_2, C_3H_8, CO and NO peaks.

Results and discussion

The mineralogical characterization by XRPD revealed the presence of two natural zeolite species: clinoptilolite (typical formula $(Na,K)_6$ $[Al_6Si_{30}O_{72}]20H_2O$) and mordenite (typical formula $(Na_8[Al_8Si_{40}O_{96}].24H_2O)$) [12]. The XRPD pattern of clinoptilolite agrees with that observed in the PDF 39-1383.(d values in Å at 9.874,100 %; 22.461, 63 %; 22.775, 48 %; 30.052, 47 %; 19.070, 19 %) whereas mordenite is characterized by XR-signals at d values (in Å) at 9.754,100%; 22.205, 70 %; 25.575, 45 %; 27.680, 40 %; 26.266, 35 %) in accordance with the reference PDF 29-1257. The sharp line at 2 θ =26.65º [13], overlapped with that of mordenite, reveals the presence of quartz as very crystalline phase despite it was observed as minor component by petrography study.

Scanning electron microscopy measurements show typical morphology for both zeolite species (fibrous for MOR and tabular for CLI) as it is observed in figure 1. Likewise, zeolite tuff is characterized by a low BET specific surface area (values between 15-23 m^2/g), typical of mesoporous natural samples.

Chemical analysis by ICP-AES technique for major elements is given in Table 1.

On the basis of zeolites stoichiometry, the relatively higher affinity of CLI toward the big cations and considering a maximum content of quartz of 10 % (by petrography study), a CLI/MOR ratio close to one is estimated.

A partial exchange of alkali and earth-alkali elements by NH_4^+, under soft chemical condition, is observed. Thermal treatment at 400ºC leads to the NH_3 evolution, although the total elimination is observed at ~ 500ºC, in the course of the indirect method to form an acid-zeolite.

Table 1: ICP-AES data for major elements expressed as oxides (%w/w).

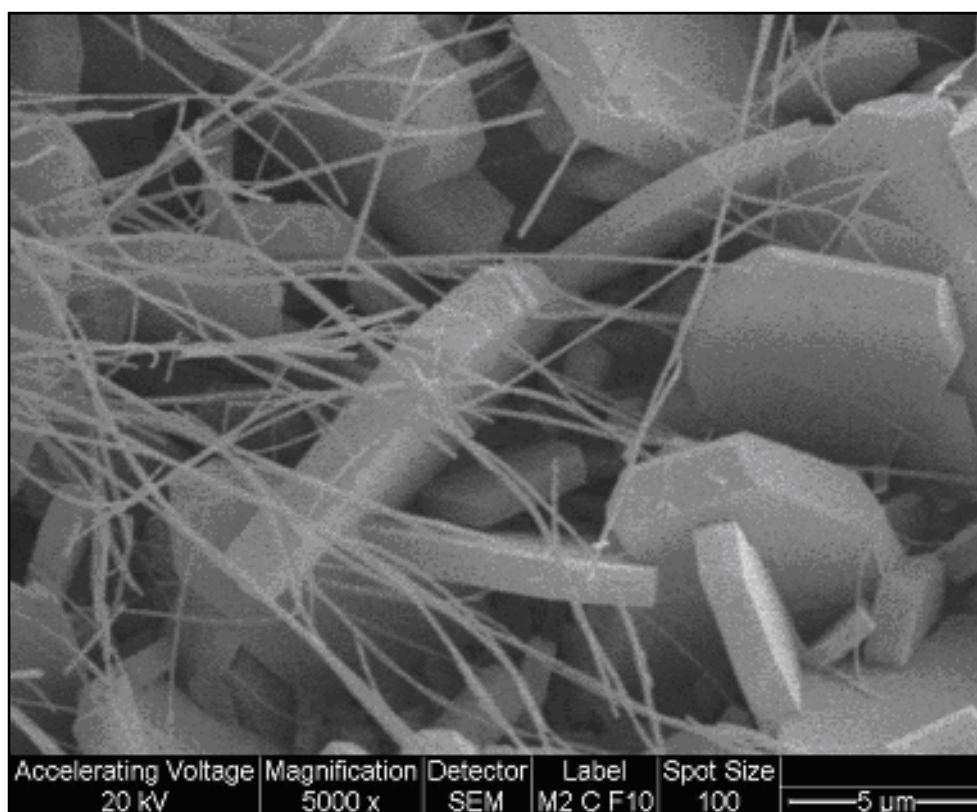| SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	H_2O
67.22	0.14	11.68	0.68	0.02	0.42	1.21	3.95	1.61	0.03	12.8

Figure 1. Typical SEM photograph of the studied zeolite mixture.

Figure 2 shows the comparative FTIR spectra of the natural zeolite (a), a sample partially exchanged by ammonium (b) and an exchanged sample treated at 400ºC (c).

The characterization of zeolites by FTIR technique is based on the presence of bands in three regions. A higher one corresponds to the OH stretching modes (3650- 3450 cm^{-1}) with an additional band at 1626 cm^{-1} for the H-O-H bending of the water molecules. The middle zone (1200-900cm^{-1}) is characterized by strong bands attributed basically to the TO_4 (T=Al,Si) stretching modes whereas the corresponding bending modes of the 3D covalent arrangement are observed below 700 cm^{-1} [14]. Ammonium exchanged samples present additional bands at 3200 and 1400 cm^{-1} respectively, according with the local symmetry [15]. On the other hand, ammonium modified zeolites treated at 400ºC reveal the presence of residual NH_4 groups as well as a reinforcement of

the T-O bonds (shifting from 1059 to 1076 cm^{-1}) due to the rupture of multiple H bonds. Likewise, the presence of a strong OH bond (3700 cm^{-1}) is also associated to the effect of NH$_3$ elimination.
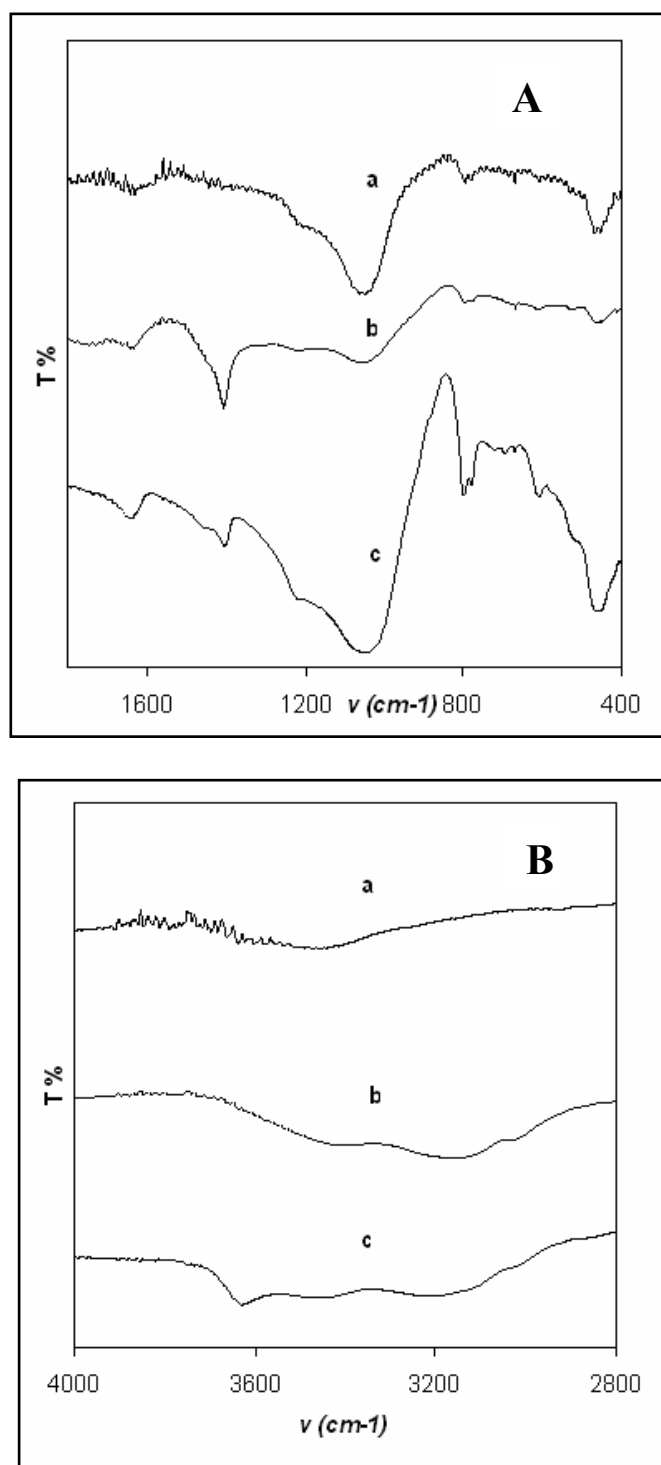

Figure 2. FTIR spectra between 2000-400 cm^{-1} (**A**) and 4000- 2800 cm^{-1} (**B**) respectively: a) natural sample, b) sample exchanged by NH$_4^+$ c) sample exchanged by NH$_4^+$ and treated at 400ºC

The modified zeolites are treated with aqueous solutions containing Co(II) and Rh(III) ions. According to experimental section, the procedure is mild, (contact with diluted solutions in an unique step at RT). The EDS-EDAX analysis reveals that the original Si/Al ratio remains constant (~5) after all treatments. For the ammonium exchanged zeolites, the alkalis as well as the Ca contents decrease (~ 50 and ~ 70 % respectively), revealing clearly the cation exchange of more accessible and less selective cation species. Bulk chemical analysis of cobalt performed by AAS, is 0.38% w/w, whereas the Rh content is 0.25% w/w in all cases. The cobalt content in exchanged zeolite mixture is lower than that reported for a pure clinoptilolite sample (in similar operative conditions), pointing out the structural effect on the exchange properties [11].

The surface EDS-EDAX analysis given in table 2 shows higher values for the cobalt and rhodium contents respect to the bulk ones. Regarding to cobalt values, they can be attributed not only to the metal incorporated by cation exchange process (diminution of Mg, Na and Ca) but also to the metal dispersed as clusters on the surface. For the bimetallic sample, the deposited oxide Rh phase seems to overlap the remaining elements owing to the Rh impregnation by incipient wet technique.

Table 2: EDS data of elements (%w/w) for natural and modified samples

| Element	Natural sample	NH₄-CLIMOR	Co-CLIMOR	Rh-Co-CLIMOR
Al	15.02	15.77	15.59	15.55
Si	76.22	79.84	79.61	79.44
Mg	0.60	0.71	0.58	0.56
Na	2.78	1.53	1.31	1.22
K	3.29	1.56	1.54	1.49
Ca	2.08	0.58	0.51	0.39
Co	-	-	0.86	0.65
Rh	-	-	-	0.70

Figure 3 shows "in situ" comparative XR-diffraction patterns of Co-CLIMOR up to 800ºC. No appreciable structural change is observed in the studied range of temperature.

Figure 4 shows the thermo-gravimetric study of the metal modified zeolites, including the natural mixture as comparison. Two zones of weight loss are clearly observed. The first one (up to 300ºC) corresponds to the loss of hydration water whereas the second one, in the 400-500ºC range, can be associated to the loss of residual ammonium species.

The deamoniation process which leads to the generation of Brönsted acid sites (in the course of the acid zeolite formation) [16] is schematically as follows:
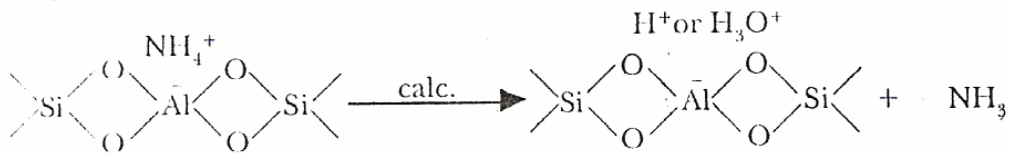
At ~ 450ºC, the 3D arrangement is affected, with a clear diminution of the local symmetry, particularly that corresponding to the tetrahedral Al, in agreement with the following scheme:
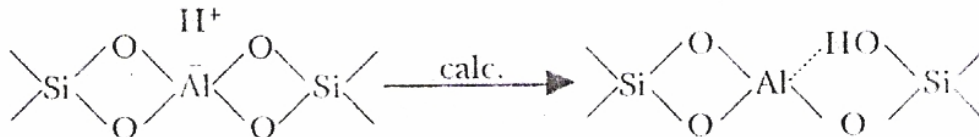
Finally, the dealumination or segregation of aluminium species occurs at higher temperature.
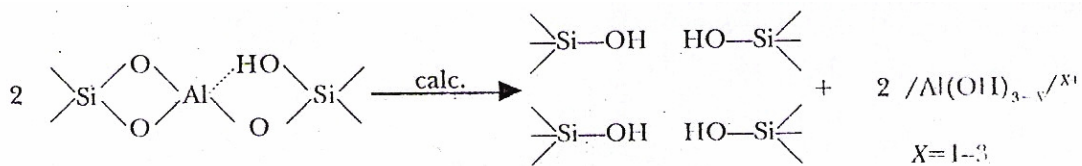
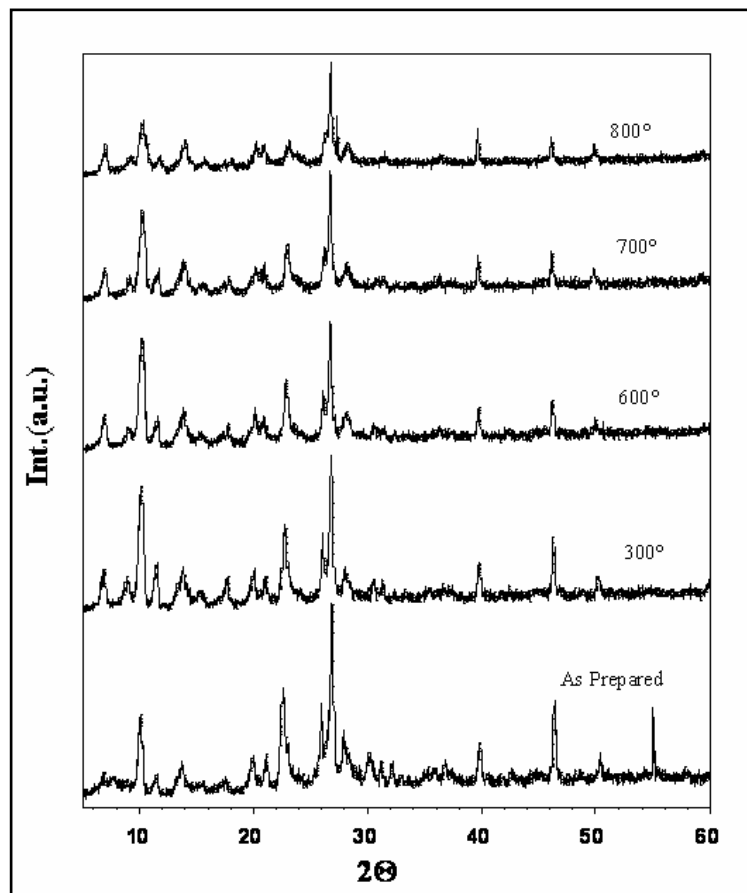This process is the beginning of the lattice collapse [16].

Figure 3. Comparative "in situ"XRPD patterns of exchanged Co-CLIMOR.
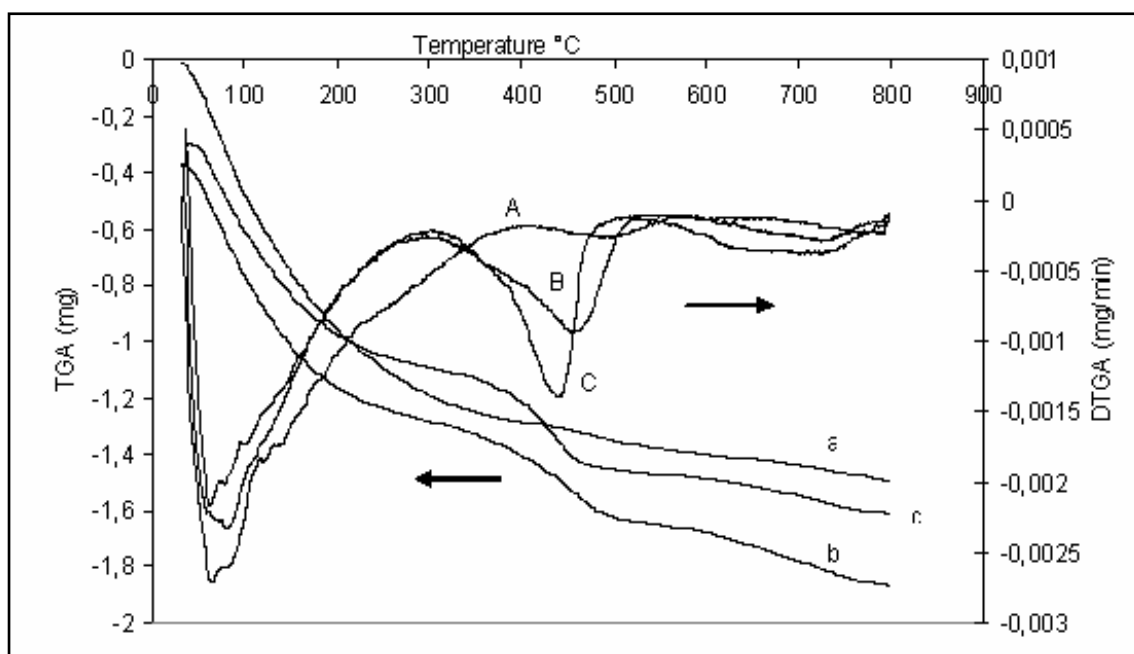
Figure 4. TGA-DTGA patterns of natural (A-a), monometallic (B-b) and Bimetallic (C-c) zeolites.

The study of the Co and Rh reducibility is performed by means of the TPR technique. Figure 5 shows the TPR patterns of natural and modified samples, previously heated at 500ºC. Whereas the natural material does not present any signal, the Co and Rh modified zeolites show a series of peaks in the middle temperature zone. The Co exchanged samples are characterized by a broad band located between 400 and 650ºC (maximum at ~ 565ºC). On the other hand, TPR signals of CoO and Co_3O_4 , reported in literature, appear in the 300-400ºC region [17]. The comparison suggests a strong Co-matrix interaction.

On the other hand, Rh-zeolite presents two signals at 140 and 190 ºC. The Rh_2O_3 literature TPR pattern is characterized by a unique signal at 135ºC [17]. The comparison reveals the presence of two types of Rh species: the first one similar to that observed in the free oxide whereas the second one, at higher temperature, can be attributed to Rh species with a weak surface interaction.

The bimetallic system presents a more complex behavior with four reduction zones. The first one (between 50 and 300 ºC) is attributed particularly to the Rh (III)-Rhº process. The following two zones (around 400 and 600ºC), characterized by a series of weak and undefined signals, can be assigned to the reduction of Co species with different interaction, as it is observed in other supported systems [18]. The inductive Rh effect, affecting the Co redox properties, is clearly observed in this region. The last reduction zone (temperature higher than 780ºC) is associated to a Co species of very strong interaction with the support.
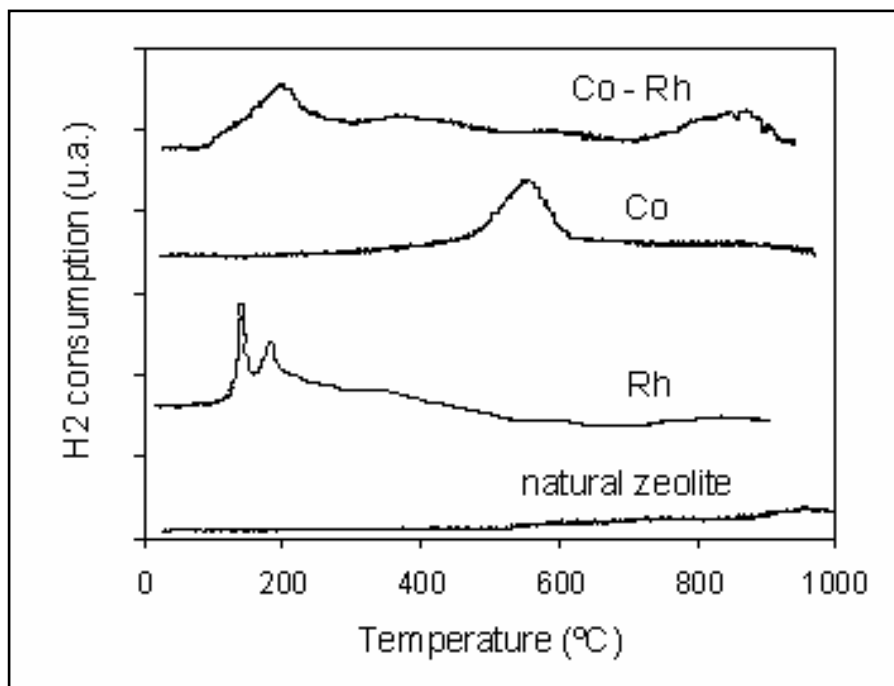
**Figure 5.** TPR patterns of natural, mono and bimetallic zeolites.

Potentiality of the system in the catalysis field

Modification and characterization of modified natural zeolites are useful to analyze the potentiality of mineral systems in order to develop new and lower cost materials. In this context, the metal modified zeolites (heated at 500ºC) are proved as catalysts in the selective catalytic reduction (SCR) process for the NO elimination. Details of the catalytic procedure are given in the experimental section.

The following reactions are useful to estimate the conversion for the principal NO - N_2 process:

$$NO + 1/2\ O_2 \rightarrow NO_2$$

$$10\ NO_2 + 2\ C_3H_8 \rightarrow 5\ N_2 + 6\ CO_2 + 8\ H_2O$$
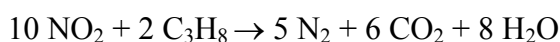
However, there is a secondary and competitive reaction for which the propane concentration decreases:

$$C_3H_8 + 5\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O$$
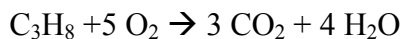
The conversion for the NO reduction is calculated in terms of N_2 production. This is given by the expression $X_{N2} = 2[N_2]/[NO]$ whereas the propane conversion is calculated as $X_{CO2} = 1/3\ [CO_2]/[C_3H_8]$ where $[N_2]$ and $[CO_2]$ are gas-phase concentrations after reaction and $[NO]$, $[C_3H_8]$ are feed concentrations.

The catalytic activity, evaluated from the NO to N_2 conversion vs. temperature, is observed in Figure 6.

The untreated sample presents an activity close to 5% at 550ºC (not shown in the figure), while the Co-CLIMOR sample shows a conversion of 42 % at 530ºC. The mechanism for which Co in an inert matrix is effective to reduce nitrogen oxides from pollutant sources has been analyzed in literature [19-21].
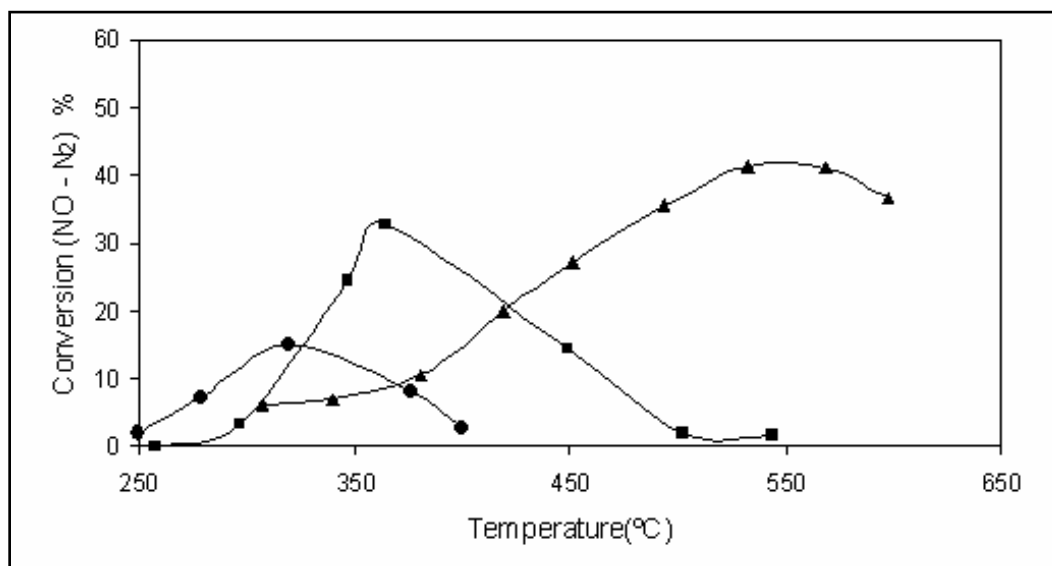
Figure 6. NO$_x$ - N$_2$ conversion for: ▲) Co-CLIMOR, ●) Rh-CLIMOR and ▪) Rh-Co-CLIMOR.

Likewise, the Rh modified zeolite reaches the lower conversion (~ 15 % at 320ºC), whereas the behavior of the bimetallic system is intermediate between that observed in both monometallic phases, with a conversion of 35 % at 380ºC. So, Rh-catalysts are characterized by the good activity at lower temperature. This is interesting due to the operational temperature range of an exhaust pipe (lower than 500 ºC). However, the content of the noble metal also affects the secondary reaction, as it is observed in Figure 7, where the propane-CO$_2$ oxidation is represented. While the propane to CO$_2$ conversion is lower than 5% using the cobalt modified zeolite at 400ºC, the presence of rhodium increases this value to 100%. Hence, the decrease of the NO conversion above 400ºC is attributed to the competition between the NO SCR and propane combustion reactions, with a considerable diminution of propane concentration. For this reason, the Rh content is a parameter that requires an adequate selection to improve the system performance.
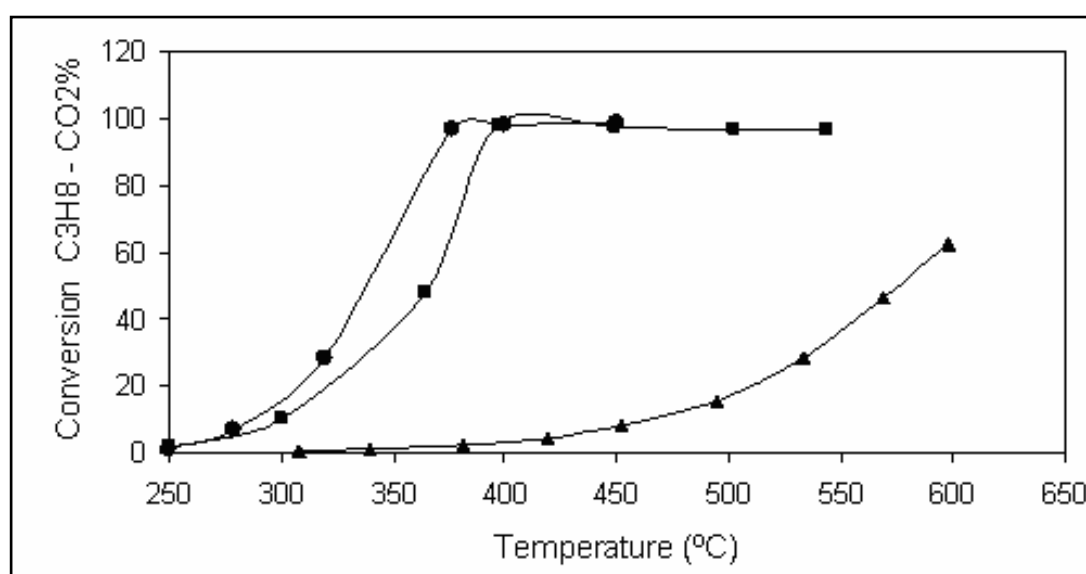

Figure 7. Propane-CO$_2$ conversion for: ▲) Co-CLIMOR, ●) Rh-CLIMOR and ▪ Rh-Co-CLIMOR

Conclusions

Natural and modified zeolite mixture, constituted by clinoptilolite and mordenite were studied and characterized by means of physicochemical techniques.

This study reveals the convenience of the soft chemical modifications to give stable materials containing Co(II) and Rh(III) metals. The treatment offers good perspectives for mineral species from Argentinean deposits and seems to be a simple and low cost technological alternative in the Selective Catalytic Reduction (SCR) of NO by propane.

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