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Co-Rh modified natural zeolites as new catalytic materials to oxidize propane and naphthalene from emission sources

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Abstract: Natural zeolites as a raw material to prepare catalytic precursors for the oxidation reaction of linear and poly-aromatic hydrocarbons are reported in this work. The process consisted in the formation of mono- and bi-metallic species containing Co and Co-Rh on natural zeolite tuffs. The materials are analyzed by different physicochemical techniques and used as catalysts for propane and naphthalene oxidation in emissions sources. Comparatively, Rh-zeolites are the most active catalysts for propane conversion. In this case, the formation of mixed oxides seems to be conditioned by surface properties. It could also be suggested that the Rh incorporation on a non-active phase in bimetallic catalysts impacts the effectiveness of the system. In addition, the NO presence increases the activity of bimetallic materials. Rh-Co zeolite systems markedly influence the naphthalene combustion temperature. Whereas in the absence of a catalyst a conversion rate of 50% and 100% is reached at 430 °C and 485 °C, respectively. It is interesting to observe that for RhCoCli-Mor and RhCoCli catalyst the 100% conversion is reached at 250 °C.

Keywords: natural zeolites, Cobalt, Rhodium, hydrocarbons combustion, catalysis

1 Introduction

Natural and synthetic zeolites are reported in literature as effective and widely used materials in industrial processes, particularly related to environmental control and catalysis [1-2]. In the catalysis field, the incorporation of an active species into the zeolite framework, by high cation exchange capacity and selectivity, is particularly useful in the design and development of new catalytic materials to apply in many organic and inorganic reactions [2].

From the structural point of view, the three dimensional zeolite frameworks are generated by the connection of the SiO_4 and AlO_4 tetrahedral species, with formation of channels and pores of molecular-dimension [3]. The Al-Si substitution leads to a negative charge, balanced by extra framework cationic species, which, as hydrated species are located in specific sites of the lattice, presenting a weak interaction with the covalent framework.

Natural zeolites are particularly interesting because although the specific surface is lower than the synthetic materials, the low cost and abundance drive to profitable catalytic materials, allows for optimizing properties such as adsorption, ionic exchange and reactivity.

This paper reviews two zeolite tuffs from Argentina deposits that were analyzed as raw materials, with the purpose of preparing new and cost-effective catalysts by a simple chemical modification. One of the samples was a clinoptilolite-rich tuff, and the other one was a mixture of (~1:1) clinoptilolite and mordenite.

Clinoptilolite has the $(Na,K)_6(Al_6Si_{30}O_{72})$ 20 H_2O as a basic formula. It is structurally characterized by 2D view channels. Channel A (formed by 10-member rings, free diameters 0.44 x0.72 nm) and channel B (8-member rings of free diameters 0.41 x 0.47 nm) are parallel to each other while channel C (8-member rings of free diameters 0.40 x 0.55 nm) intersect both A and B channels [4]. Clinoptilolite shows exchange selective capacity toward low charge density cations.

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Mordenite, with a general formula $Na_8Al_8Si_{40}O_{96}24{\bullet}H_2O$, has essentially a two-dimensional channel system with a more complicated crystal structure. Channel A, formed by the assemblage of 12-membered rings, are elliptical with free dimensions 0.65 x 0.70 nm, while channel B are 8-member rings with free diameters 0.26 x 0.57 nm. Channels A and B are interconnected via perpendicular channel B tubes, in the form of small side pockets [4]. Both zeolite types present a Si/Al ratio close to 5 and low anionic field strength with a selectivity controlled by the topology [3].

The releasing of dangerous gaseous hydrocarbons, generated by the combustion process, is a serious environmental problem, that requires a permanent control to preserve the human health. These dangerous gaseous hydrocarbons are commonly emitted by vehicles and industrial processes. To avoid their emissions to atmosphere, one technological alternative is the catalytic post-combustion oxidation using converters, which act through the presence of precious metals such as Au, Rh, Pt o Pd [5-11]. Other less expensive formulations, containing transition metal oxides, are also useful for hydrocarbon oxidation reactions at a relatively low temperature. The advantages of the metal-oxide catalysts are attributed to redox properties of metals, which are in agreement with the Mars van Krevelen mechanism [9]. In this context, Co_3O_4 reveals good activity [12], however, can also promote small proportions of precious metallic species such as Au, Rh or Pt. The synergic effect is observed by the use of Co_3O_4 and/or CuO catalysts promoted with Au [13-14] and others oxides promoted with Pt, Re and Pd [15-18]. However, the addition of these metals do not always improve the catalytic performance, as observed for the Pt/CeO_2 in the naphthalene combustion [19].

Although the use of Rh/cobalt spinel catalyst is reported for different processes [20], it is scarcely studied for hydrocarbon combustion. Hence, the aim of this work was to design catalytic strategies for this process by the use of low cost natural zeolites. Bimetallic materials, rhodium and cobalt oxide/zeolite samples as well as cobalt oxide/zeolite and rhodium oxide/zeolite catalytic monophasic species were prepared using the chemical modification of clinoptilolite and a mixture of clinoptilolite-mordenite. These catalytic precursors were obtained from ammonium zeolites (by exchange of natural samples with ammonium with further heating to remove NH_3) to give acid zeolites [21-22]. This process was followed by the treatment of acid-zeolites with solutions of Co(II) and Rh(III) salts. The catalysts were obtained by a thermal treatment of metal-precursors, and then analyzed the effect and stability of active species. Samples were characterized by physicochemical techniques whereas the catalytic behavior was described by the oxidation reaction of linear and poly-aromatic hydrocarbons. Propane and naphthalene were selected as molecular models. The efficiency of these materials was studied on the basis of physicochemical characterization.

2 Materials and Methods

2.1 Materials

Two zeolite tuffs from Argentinean deposits were used as raw materials. The first one was a natural clinoptilolite (Cli) from La Rioja province (Argentina). The second one was a clinoptilolite-mordenite (Cli-Mor) mixture from a deposit located in Chubut (Argentina).

2.2 Characterization methods

Chemical bulk analysis by ICP-AES was done in the ALS CHEMEX Laboratory.

The crystalline phases were identified by X-Ray powder diffraction (XRD) analysis by using a Rigaku D-Max III diffractometer equipped with Ni-filter and Cu Kα radiation.

Energy dispersive X-ray spectroscopy (EDS) analyses were performed using a SEM Philips 505 microscope provided with an EDAX DX PRIME 10 energy dispersive X-ray analyzer.

Surface measurements were carried out with a Micromeritics ASAP 2020 using the BET method for their estimation.

The chemical determination of cobalt by atomic absorption spectrophotometry was done in a Perkin Elmer AA 3110 spectrophotometer.

Temperature programmed reduction (TPR) experiments were carried out with a conventional equipment. The TPR profiles were performed using 10% hydrogen in nitrogen (flow rate 20 mL min^{-1}) with a heating rate of 10 °C/min up to 950 °C. The sample loaded was 20 mg.

FTIR spectra were recorded in a Bruker EQUINOX 55 at room temperature in the 4000–400 cm^{-1} range. Samples were prepared as KBr discs.

2.3 Preparation of catalysts

Catalysts were obtained from the successive modification of natural species by chemical treatments.

The first step of treatment was the exchange reaction to form ammonium zeolites. Therefore, 10 g zeolitized tuff (Cli and Cli-Mor) was treated with NH_4Cl (99.5%, Anedra), 0.5 M solution in excess, at RT for 8 h with an initial stirring of 2 h. The obtained ammonium zeolites were heated at 400 °C (for 24 h) to yield acid zeolites. The catalytic precursors were prepared by the treatment of acid zeolites with diluted Co(II) acetate (99.99%, Aldrich) and Rh(III) chloride (99.98%, Aldrich) aqueous solutions as follows:

Assay I: acid zeolite samples were treated with $Co(Ac)_2$ 0.01M solution (ratio 1/4 g ml^{-1}) for 12 h.

Assay II: the acid form of each zeolite was treated with a 10^{-4} M solution of $RhCl_3$ solution until wetness to obtain a Rh content of 0.25% w/w.

Assay III: 1 g of material resulting from assay I was treated with an $RhCl_3$ solution 10^{-4} M until wetness to obtain an Rh content of 0.25% w/w, as in previous assay.

Finally, the catalysts underwent thermal treatment of metallic precursors at 500 °C for 2 h. The samples were identified as it is indicated in Table 1 and characterized by the techniques mentioned in Section 2.2.

The Rh content was 0.25% in all cases, and the Co values were 0.38 and 0.50% for materials obtained on the bases of CliMor and Cli respectively (data by AAS).

2.4 Measurements of catalytic activity

The catalytic reactions for propane oxidation were evaluated in a quartz (id=0.8 cm), fixed bed reactor, that was electrically heated. The temperature was measured by means of a K-type thermocouple which was in contact with the catalytic bed. The reaction mixture was obtained from four feed lines individually controlled (AALBORG flow controller): NO/He, C_3H_8/He, O_2/He and He to close the balance at 1 bar. The reactive gases are stirred in a mixing valve and then pass through of a four-way valve, prior to entering the reactor. The reaction flow contained 0 or 1000 ppm NO, 2000 ppm of C_3H_8 and 8% of O_2. The total flow rate was 50 mL min^{-1}. The used catalyst mass was 0.100 g. The reaction temperature was increased at rate of 1.6 °C/min from 150 to 600 °C.

The reaction products were monitored with a Shimadzu gas chromatograph, model GC 2014, and a thermal conductivity detector. The products were separated with a concentric column CTRI by Altech. This system permits identification and quantification of O_2, N_2, CO_2, C_3H_8, CO and NO.

Table 1: Identification of Catalysts according to assays performed on the zeolite samples.

Name of catalyst	Zeolite	Assay
CoCli	Cli	I
RhCli	Cli	II
RhCoCli	Cli	III
CoCli-Mor	Cli-Mor	I
RhCli-Mor	Cli-Mor	II
RhCoCli-Mor	Cli-Mor	III

The propane combustion conversion was calculated by the following reaction:

$$C_3H_8 + 5\,O_2 \rightarrow 3\,CO_2 + 4\,H_2O \quad (1)$$

and using the expression XCO_2=1/3 $[CO_2]/[C_3H_8]$, where $[CO_2]$ is gas-phase concentration after reaction and $[C_3H_8]$ is feed concentration. The carbon balance in the measurements was better than the 98%.

The catalytic activity for naphthalene oxidation was evaluated in a fixed-bed quartz reactor containing 0.100 g of catalyst. The oxidation was determined using a mixture of 10% O_2, 90% He and 150 ppm of naphthalene. The total flow rate was 30 mL min^{-1}. The naphthalene concentration used in this work was used in other reports [23, 24]. The naphthalene conversion was calculated following the reaction:

$$C_{10}H_8 + 12\,O_2 \rightarrow 10\,CO_2 + 4\,H_2O \quad (2)$$

by using the expression XCO_2= 1/10 $[CO_2]/[C_{10}H_8]$ where $[CO_2]$ is gas-phase concentration after reaction and $[C_{10}H_8]$ is feed concentration.

To ensure a constant vapor pressure of naphthalene the feed stream passes through a saturator, in a water bath and is kept at 25 °C, where the naphthalene is placed. The rest of the flow system was held at a higher temperature to avoid the undesired reverse sublimation of naphthalene. For each temperature, the result was an average of four measurements. In all cases the sampling procedure is performed once the naphthalene vapor pressure was stabilized.

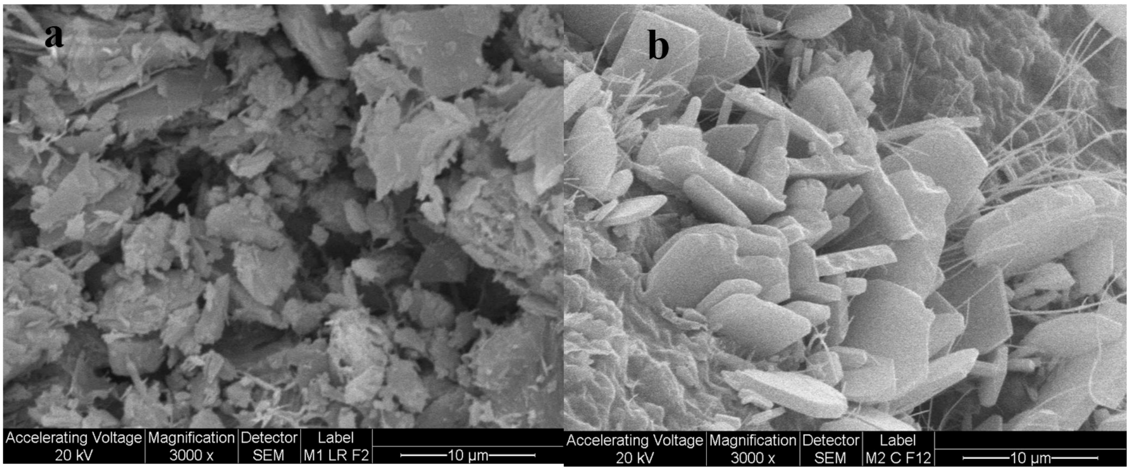

Figure 1: SEM micrograph of original samples (3000x, 10 µm): a) Cli, b)Cli-Mor.

Table 2: ICP-AES chemical analysis (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
Cli	66.99	0.16	13.39	0.87	0.01	0.99	2.54	3.53	1.48	0.04	10.08
Cli-Mor	67.22	0.14	11.68	0.68	0.02	0.42	1.21	3.95	1.61	0.03	12.8

3 Results and Discussion

3.1 Physicochemical Characterization

Table 2 gives the chemical analysis of major elements (expressed as oxides) for zeolite samples from the ICP-AES technique. Both natural samples presented a Si/Al ratio close to 5.

X-ray diffraction patterns of the original samples show the presence of clinoptilolite and a mixture of clinoptilolite and mordenite, in agreement to the PDF 39-1318 and 29-1257 respectively [21]. The x-ray lines of quartz were also identified in a minor proportion by the most intense signal at 26.65 ° of 2θ (PDF 46-1045). No additional lines or appreciable changes in the patterns of modified samples were observed, and revealing the structural stability of the covalent framework in the complete temperature range (up to 800 °C) [21-22]. The presence of vitreous phase is clearly observed in the Cli sample, according to analysis by petrography [21].

The morphology of the original samples were observed in the SEM images of Figure 1. The small clinoptilolite euhedral crystals (Figure 1a) differ from the well developed individual clinoptilolite "coffin shaped" crystals (Figure 1b), where typical thin and elongated fibers of mordenite are observed. The morphological differences between both samples can be attributed to the crystallization process of Clinoptilolite found in natural conditions.

Table 3: Surface properties of original zeolite samples

Zeolite	BET Specific surface area $m^2\ g^{-1}$	$V_{pore\ total}$ ml g^{-1}	S_{ext} $m^2\ g^{-1}$
Cli	11.0	0.043	8.4
Cli-Mor	22.6	0.071	15.3

On the other hand, Table 3 reveals a comparison of main surface characteristics of both samples. The lower textural values for Cli sample can be attributed to the presence of the vitreous phase.

The transformation to acid zeolites, as a previous step for the Co and Rh chemical modification, increased the BET specific surface area. In fact, the new values were 14.5 $m^2g^{-1}$and 41.8 m^2g^{-1}, (an increase of about 32 and 85%), for H-Cli and H-Cli-Mor respectively.

Likewise, the FTIR spectra of the original and modified samples display bands in the same region. The strongest signal can be assigned to the asymmetric stretching vibrations of the internal Si-O-(Si,Al) bonds centered between 1000-1058 cm^{-1}, although shoulders are above 1200 cm^{-1} could be also suggested. Bands below 770 cm^{-1} could be assigned to the O-(Si,Al)-O vibrational modes whereas the presence of a broad band in the 3500 cm^{-1} region could be assigned to O-H stretching of water and

Table 4: Comparison between the Co and Rh chemical analysis EDS (surface) and AAS (bulk), for mono and bimetallic catalysts (precursors heated at 500 °C).

	RhCli	CoCli	RhCoCli	RhCli-Mor	CoCli-Mor	RhCoCli-Mor
Co by (EDS)	-	0.8	0.74	-	0.52	0.47
Rh by (EDS)	0.52	-	0.99	0.49	-	1.29
Co by AAS		0.50	0.50		0.38	0.38
Atomic ratio Co/Rh by EDS			1.3			0.6

hydroxyl groups [21]. In relation to the FTIR behavior of ammonium modified zeolites, the presence of NH_4^+ modes was observed through splitting of the H-N-H bending mode at 1397-1432 cm^{-1} as well as the broadening and shifting toward lower values of the intense band originally centered around 3500 cm^{-1} [21]. By heating to 400 °C, the FTIR spectra showed a signal disappearance at 1400 cm^{-1} and the shifting of the most intense band toward higher values. (1086 cm^{-1} for Cli and 1076 cm^{-1} for the Cli-Mor mixture) This can be attributed to the reinforcement of (Si,Al)-O bonds by breakdown of H- bonds. After treatment with Co(II) and Rh(III) salts and a new thermal treatment at 500 °C, the FTIR spectroscopy suggests the preservation of the structural atomic arrangement, in agreement with XRD results.

The treatments with transition metals have not modified the areas of the materials, probably because they are in very low concentration [21].

For the modified species, the comparison between bulk and surface Co and Rh contents by AAS and EDS respectively are given in Table 4.

The values suggest that the interaction between metals and zeolites occurred at the surface level. However, differences between bulk and surface chemical data either for mono-and bi-metallic systems could be associated to the preferential formation of metallic clusters, favored by substitution processes according to the interaction with different structural lattices. Although the Rh content is similar in both samples obtained by the experimental procedure, these aspects together with particle size and surface properties affect the formation and distribution of active species.

The development of Co(II), Co(III), Al(III) and Rh(III)) mixed oxides (particularly spinel type) can be expected according to cationic sizes and possibilities of substitution. Likewise, the surface properties as well as OH sites generated in previous treatments surely play an important role in the formation of different types of oxides. In this sense, precious metal substitution result in an increase of lattice parameters enhancing the activity of catalysts [20]. Similarly it has also been observed in some Co-supported systems employed for the propane oxidation that the lower surface area and promotes the agglomeration of metal-oxide phases as larger crystals with a little interaction with the surface support [12]. So, from surface results, it was expected that the interaction between Co and zeolite lattice was higher in the Cli-Mor sample. Hence, the probable formation of Al(III)-Co(III) substituted spinel phase could be higher in this case. On the other hand, further treatment with Rh led to the formation of highly dispersed Rh oxide on the surface, although the Co(III)-Rh(III) substitution could not be discarded [20]. An opposite behavior can be suggested for the zeolite sample with the lowest surface (Cli), according to the sequence of the chemical treatment, which favored the formation of Co-O and Rh-O spinel phases (overlapped and substituted). These aspects were in agreement with the Rh/Co atomic ratio of 0.6 and 1.3 for RhCoCli-Mor and RhCoCli respectively.

Considering the use of these catalysts in the oxidation reactions, the activity of the metallic species is governed by the redox availability. Therefore, the relationship between the oxidation activity and the oxygen mobility could be analyzed through TPR profiles of chemically modified samples, and are shown in Figure 2.

Natural zeolites do not show a significant consumption of hydrogen. It is well known that Co_3O_4 bulk spinel phase reduces in two steps: the first phase (Co(III)-Co(II)) between 250 and 350 °C, and the second phase (Co(II)-Co^{o}) occurs between 350 and 470 °C [25]. The reducibility of the exchanged Co/zeolite structure depends on the metallic location in the lattice: at the surface level the temperature reaches values between 500 and 600 °C whereas in channels or pores the temperature can be considerably higher than 700 °C [22]. By comparison, the TPR profile of isolated Rh_2O_3 is characterized by one signal at low temperature (135 °C) [26]. The qualitative TPR profiles of CoCli and CoCli-Mor were similar, with a signal in the 500-600 °C region, although the CoCli reduction process started at lower temperature. However, the reduction

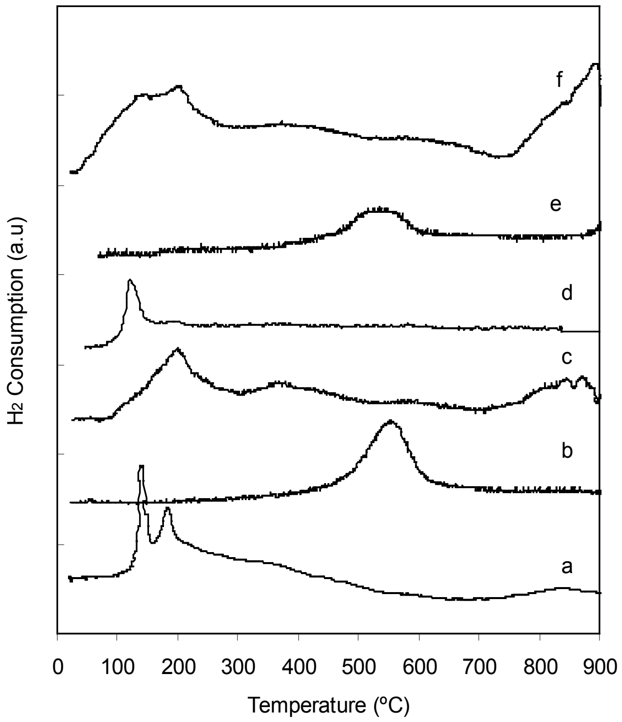

Figure 2: TPR profiles of: a) RhCli-Mor, b) CoCli-Mor, c) RhCoCli-Mor d) RhCli, e) CoCli, f) RhCoCli.

integrated area for this catalyst was lower than that observed for the CoCli-Mor (with lower cobalt content on surface). The effect can be attributed to different oxide phases, a more homogeneous distribution of active sites and consequently different accessibility to the reducing gas.

The TPR profiles of the Rh-monometallic systems shows appreciable differences. The RhCli-Mor presented two signals at 143 °C and 185 °C, RhCli was characterized by one signal at 125 °C, in a similar way to that observed for pure Rh_2O_3 oxide. Among the factors that affect the reduction of Rh(III) in the mixture of zeolites, includes the dispersion magnitude and the possible Al-Rh substitution can be mentioned, thus suggesting different availability of active sites. Likewise, as it is observed in Figure 2, the reduction area is higher for the RhCli-Mor with respect to that observed for RhCli, reinforcing the concept that the reduction agent is more accessible in the first sample.

The behavior of bimetallic systems clearly demonstrates the promoting effect of rhodium, enhancing clearly the cobalt reducibility. Strong peaks at 204 °C and 207 °C for RhCoCli-Mor and RhCoCli respectively with weak signals between 200 and 700 °C could be related to the formation of mixed oxides containing both metals in sites of different reducibility [20].

3.2 Catalytic results and general discussion

Figure 3 shows the combustion profile of propane vs. temperature using the catalysts. The propane combustion without catalyst, not shown in the figure, occurs at very high temperature, reaching 50% conversion at 620 °C.

The natural zeolites do not show activity. In the general context, CoCli and CoCli-Mor catalysts presented the lowest activity. This can be related to TPR results; in which both cases the availability of active species occurred at higher temperature.

RhCli-Mor and RhCli catalysts are both very active, reaching a conversion of 50% at 300 and 360 °C respectively. Comparatively, the activity can be associated to Rh-O availability. Although the Rh contents are similar in both catalysts, Rh species are more effective in mixture of zeolites. This fact can be associated to the different structural properties of both zeolites. Likewise, the higher specific surface of the Cli-Mor zeolite allows a higher Rh dispersion and consequently the RhCli-Mor sample is the most active catalyst.

It is evident that monometallic catalysts are more effective when the active phases are supported over the Cli-Mor zeolite mixture. This can be attributed to the higher superficial area of this material. However, the effect of support structure is not observed for the bimetallic systems.

Catalytic behavior for RhCli and RhCoCli was similar, although the Rh content on the surface was lower in the first sample. The synergic effect between both metals seems not to be effective in propane oxidation. This can be attributed to the incorporation of the precious metal in the non-active oxide containing cobalt. In relation to this conclusion, it is reported that combustion reactions of short chain hydrocarbons are more effective when active species are segregated as free oxides [12, 24].

Finally, the activity of RhCoCli-Mor is lower, although Rh content at surface level was higher. This can be associated to a higher possibility to form non-active cobalt –rhodium substituted mixed oxides.

Figure 4 shows the effect of NOx effect in propane combustion, by using RhCoCli and RhCoCli-Mor. This effect was studied by adding 1000 ppm in the feed stream. NO is a gas which usually is found in emissions of combustion products, affecting the catalytic activity. In the case of both catalysts, the NO presence slightly increased the activity. This result was attributed to the formation of N-oxide species, such as NO_2, with an oxidant activity higher than that of O_2. The effect is more noticeable in RhCoCli-Mor, revealing that the catalyst based on the use

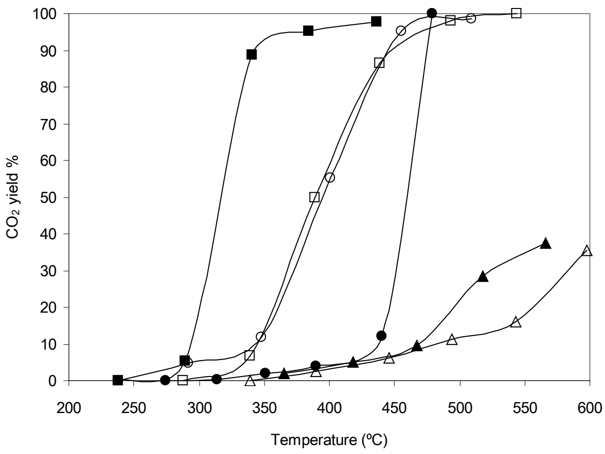

Figure 3: Propane combustion vs. temperature for: Δ) CoCli, ▲) CoCli-Mor, ☐) RhCli, ■) RhCli-Mor, ○) RhCoCli, ●) RhCoCli-Mor. Reaction conditions: catalyst 0.100 g, total flow 50 mL min^{-1}, 2000 ppm of C_3H_8, 8% of O_2 and He to balance.

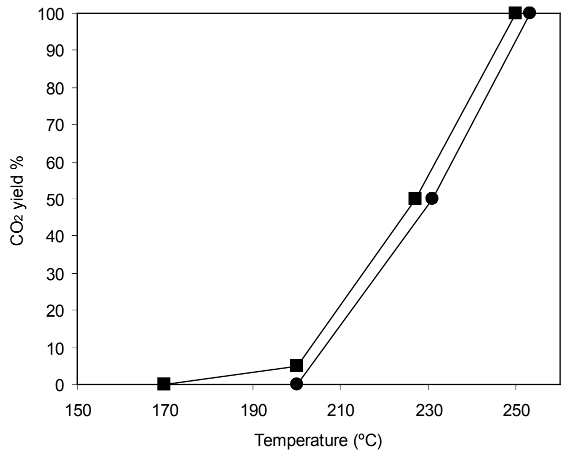

Figure 5: Naphthalene combustion vs. temperature for: RhCoCli-Mor and RhCoCli. Reaction conditions: catalyst 0.100 g, total flow 30 mL min^{-1}, 10% O_2, 90% He and 150 ppm of naphthalene.

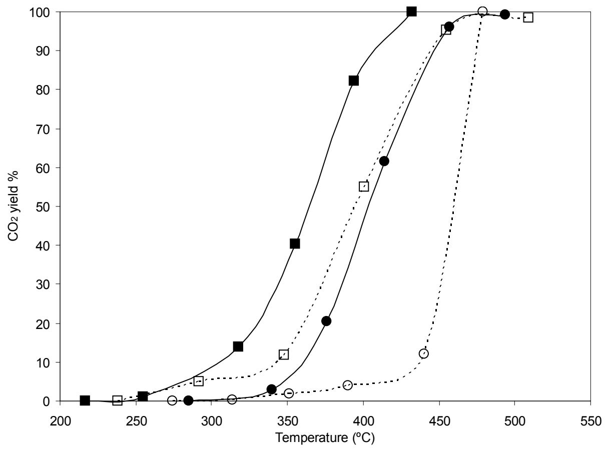

Figure 4: Effect of NOx in the propane combustion, by using RhCoCLI and RhCoCli-Mor. With NO: ■) RhCoCli, ●) RhCoCli-Mor, without NO: ☐) RhCoCli, ○) RhCoCli-Mor. Reaction conditions: catalyst 0.100 g, total flow 50 mL min^{-1}, 0 or 1000 ppm NO, 2000 ppm of C_3H_8, 8% of O_2 and He to balance.

of Co-Rh natural zeolites is useful in similar conditions to that presented in emission resources.

For comparative purposes and considering results obtained for propane, the catalytic activity for naphthalene combustion was analyzed. Figure 5 shows the naphthalene-CO_2 conversion vs. temperature, by using RhCoCli and RhCoCli-Mor catalysts. Whereas in absence of catalysts a conversion of 50% and 100% is reached at 430 °C and 485 °C respectively, it is interesting to observe that for the bimetallic catalyst the 100% conversion is reached at 250 °C, revealing an advantage of using the simple strategy of catalyst preparation by means of a chemical treatment on the basis of low-cost raw materials. For comparative purposes, it was commented that literature reports data of similar activity for catalytic systems based in the use of synthetic high cost supports (27-29).

By comparison, the activity seems to be different for both types of hydrocarbons. The mechanism for poly-aromatic hydrocarbon combustion shows a prevalence of a surface effect. In this way, the effect of zeolite structural type affects the catalytic activity for naphthalene oxidation. RhCoCli-Mor was slightly more active than RhCoCli. This behavior is different to that observed for propane oxidation where the new cobalt-rhodium supported phases were not active over the Cli-Mor zeolite. The naphthalene molecular complexity minimizes differences, through a poly-aromatic structure, which could be explained by a different reaction mechanism for the catalytic cycle.

4 Conclusions

Comparing with literature data of other catalysts used in similar experimental conditions (reactant concentrations, GHSV, etc.), it was possible to conclude that catalysts reported in this work for combustion processes of selected propane and naphthalene hydrocarbons are active materials. In fact, RhCli-Mor and RhCli presented the highest performance for propane oxidation, reaching conversion temperatures about 300 °C lower than those observed for the oxidation without catalyst (620 °C), the Rh -Co synergic effect of bi-metallic systems seemed to be slightly less effective, which could be explained by the formation of mixed oxides where Rh is incorporated in non-active oxide phases. Likewise, the catalytic behavior with NO presence increased the activity, according to comparative study by using bimetallic materials. On the other hand the Rh-Co-zeolite systems affected more effectively the temperature of naphtalene combustion, reaching a conversion of 100% at 250 °C. It is evident that the catalytic cycle for poly-aromatic structure can be explained by means of a different reaction mechanism. All these aspects, together with the low cost of raw materials and simplicity of activation by means of chemical modification, are very promising factors to reduce the concentrations of volatile linear and poly-aromatic hydrocarbon in emissions.

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