Promoting Effect of Pt on CoZeolites upon the SCR of NO_x

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1. INTRODUCTION

The promoting effect of Pt incorporated to Cozeolites (viz., mordenite, ferrierite, ZSM-5, and Y-zeolites) on the selective catalytic reduction (SCR) of NOx with CH4 was studied. The PtCo bimetallic zeolites showed higher NO to N₂ conversion and selectivity than the monometallic ones under all reaction conditions tested. The Y-zeolite based samples which were inactive both in the mono and bimetallic samples constituted an exception. The promoting effect was a function of the zeolite type and, for a given zeolite, of the pretreatment of the catalysts and Pt loading. The best results were obtained for a 0.5% Pt loading after reduction of the samples in H₂ flow for 1 h at 350°C. Under dry conditions Pt_{0.5}Co_{2.0} mordenite converted 60% of NO to N2 at GHSV of 100,000 h⁻¹ with a CH4/NO ratio of 3 at 500°C and 2% oxygen in the feed stream. The specific activities given as molecules of NO converted per total metal atoms per second at 500°C were 16.5 10^{-4} s⁻¹ for Pt_{0.5}Co_{2.0}Fer, 13 10^{-4} s⁻¹ for $Pt_{0.5}Co_{2.0}Mor$, and 4.33 $10^{-4} s^{-1}$ for $Pt_{0.5}Co_{2.0}$ ZSM-5. The incorporation of Pt also shows a positive effect in the stability of the samples under wet reaction conditions. The XPS results revealed that in the calcined samples most of the Co²⁺ and Pt²⁺ was located at exchange positions. After reduction no changes in the binding energies (B.E.) were observed in samples with low Pt loading. For higher contents (viz., 1 to 5 wt%) the B.E. characteristics of Co° and Pt° , as well as Co^{2+} and Pt^{2+} , were detected. No evidence of alloy or intermetallic compounds at the surface level was observed. The incorporation of Pt also promoted the Co reducibility in the zeolitic matrix. The greater reducibility and a shift of the maxima in the temperature-programmed reduction profiles suggest a Pt-Co interaction inside of the zeolitic channels. The solid that the reacting mixture initially "sees" has Co° and Pt° metallic particles highly dispersed in the zeolitic matrix, together with Co^{2+} . Some Pt^{2+} and protons generated during reduction also appeared. Such species remained after reaction but some reorganization occurred. In order to get an efficient catalysts for nitric oxide abatement it is necessary for such species to be in intimate contact. A synergetic effect among the different sites could be responsible for the high activity of the bimetallic zeolites. © 1998 Academic Press

Key Words: selective catalytic reduction; NO_x; methane; zeolites; PtZeolites; CoZeolites; PtCoZeolites.

The selective catalytic reduction (SCR) of NO by hydrocarbons in the presence of oxygen excess is of great interest for the automotive industry, in which a suitable catalyst facilitates the development of the lean-burn engines technology which could significantly enhance fuel economy (1), as well as the potential use of SCR for the purification of diesel exhaust gases. It is also of interest to other industries, in which the use of hydrocarbons such as methane is an attractive alternative to the currently practiced technology, which uses ammonia as a reducing agent. Iwamoto et al. (2) and Held et al. (3) were the first ones to report that Cu-ZSM-5 is active for the selective lean NO_x reduction to N₂ by hydrocarbons. Since then, different types of catalysts with various hydrocarbons have been used with the same purpose. This has been lately reviewed by Farrauto and co-workers (4).

Within this framework the use of CH_4 as reducing agent has become particularly interesting, given the plentiful supply of CH_4 in the world and the fact that it is a common fuel used in stationary engines at power plants which are producing NO_x during the combustion process.

Li and Armor (5–7) were the first to announce a new catalytic technology based on Co-zeolites using methane to selectively reduce NO. Since then, various solids have been employed with the same purpose (8–10). They have not yet been employed due to the deactivation that such catalysts suffer in the presence of water and SO₂ (unfortunately present in the exhaust gas stream), among other causes. Noble-metal-based catalysts seem to have overcome most of these problems. However, some of them are little selective in the presence of oxygen excess. In fact, Pt and Rh exchanged in ZSM-5 (11) have a high selectivity in the absence of O₂ but when 2.5% oxygen is added to the feed, platinum is nonselective, the NO to N₂ conversion being only 3% with 25% of NO₂. Under these conditions Rh-ZSM-5 presents 25% of NO conversion with approximately 10% of NO2 at 450°C. Behaviors of Pd-based catalysts on different acid supports, including H-ZSM-5 and H-CeZSM-5, have been studied lately. Loughran and Resasco (12) and Nishizaka and Misono (13) reported a conversion of NO_x

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to N₂ of about 70% at 450°C at 1000 ppm NO, 2% O₂ in dry systems with 2000 ppm CH₄ at GHSV = 9000 h⁻¹. However, Nakatsuji *et al.* (14) found that the presence of SO₂ dramatically deteriorated the performance of Pd/Al₂O₃.

Extensive efforts have recently been made to improve both transition and noble metal catalysts, including their NO reduction activity and selectivity and more important still, their durability under real operation conditions with various hydrocarbons as reducing agents. Multivalent ions were studied as cocations to stabilize Cu-zeolites (15, 16). Similarly, bicomponent catalytic systems have been proposed to solve the problems caused by water vapor (17, 18). Other attractive catalysts are the ones reported by Kikuchi and co-workers, who found that the addition of precious metals (Pt, Rh or Ir) to In/H-ZSM-5 improves the NO conversion in the selective reduction with methane under wet conditions (19, 20). Simultaneously Gutierrez et al. (21) found that the Pt added to CoMordenite also promoted the same reaction under dry and wet conditions. In addition, Kikuchi reported a cooperative effect of Pd and Co on Pd/Co/H-ZSM-5 which shows high catalytic performance for the removal of low NO_x concentrations, even in wet atmospheres (22). Recently Iwamoto et al. (23, 24) also reported the cooperation of PtZSM5 and In, H, Zn, Ag, Ga, Mg, Ba, and Ca exchanged in ZSM5, in the SCR of NO_x when the catalysts were used in a twin reactor system with the intermediate addition of ethane into a $NO + O_2$ stream. They found that such a method increases the effectiveness of the monometallic zeolites for the said reaction.

The present work investigates in detail the effect of the coexistence of platinum and cobalt. The role of the zeolite structure (ZSM-5, ferrierite, Y-zeolite, and mordenite) in the SCR of NO_x with methane is also studied. An attempt is also made to elucidate the nature of the active sites in the bimetallic zeolites.

2. EXPERIMENTAL

2.1. Catalysts Preparation

Different zeolites such as Na-mordenite $[Na_7(AlO_2)_7 (SiO_2)_{41}]$, Na-ZSM-5 $[Na_9(AlO_2)_9(SiO_2)_{87}]$, Na-Y $[Na_{56} (AlO_2)_{56}(SiO_2)_{136}]$, and K-ferrierite $[(Na, K)_{3.7}(AlO_2)_{3.7} (SiO_2)_{32.3}]$ were used as zeolitic supports. The prepared catalysts are shown in Table 1.

2.1.1. Cozeolites

Monometallic cobalt zeolites were prepared by ion exchange using a diluted solution of $Co(NO_3)_2 0.025 M$. The support was put in contact with the solution (with a zeolite/ solution ratio of 2g/dm³), stirred for 24 h at room temperature, keeping the pH between 5 and 6 during the exchange. It was then filtered, washed, and dried in a stove at 120°C for 12 h.

TABLE 1

Prepared Solids

		Metallic content% ^a		Me/Al	
Samples	Si/Al	Со	Pt	Co/Al	Pt/Al
Pt _{0.5} Co _{2.0} Mor	5.9	2.87	0.39	0.21	0.01
Pt _{1.0} Co _{2.0} Mor	"	2.63	0.73	0.19	0.02
Pt _{3.0} Co _{2.0} Mor	"	0.14	2.39	0.01	0.05
Pt _{0.5} Co _{2.0} HMor	"	1.83	0.30	0.14	0.01
Co _{2.0} Mor	"	2.91	_	0.21	_
Pt _{0.5} Mor	"	—	0.37	—	0.01
Pt _{0.5} Co _{2.0} ZSM-5	9.7	1.62	0.61	0.18	0.02
Co _{2.0} ZSM-5	"	1.81	_	0.20	_
Pt _{0.5} ZSM-5	"	_	0.72	_	0.02
Pt _{0.5} Co _{2.0} Y	2.4	5.44	0.75	0.21	0.01
Pt _{0.5} Co _{2.0} Fer	8.8	1.80	0.56	0.19	0.02
Co _{2.0} Fer	"	1.38	_	0.14	_
Pt _{0.5} Fer	"	—	0.48	_	0.02

^{*a*} Percentage of weight in metal were determined by atomic absortion and CPS.

2.1.2. Ptzeolites

Samples with different Pt content were prepared (0.5, 1.0, 3.0 wt%); 2 g of zeolite were added to 300 ml of a Pt(NH₃)₄(NO₃)₂ aqueous solution with the desired concentration. The exchange took place under the same conditions as the Cozeolite.

2.1.3. PtCozeolites

Bimetallic catalysts were obtained from monometallic Ptzeolites with a second exchange with a Co^{2+} solution following the technique described for Cozeolites.

2.1.4. PtCoHMordenite

4 g of NaMordenite were put in contact with 2 liters of a $NH_4(NO3)_2$ 1 *M* solution for 24 h in reflux heating. They were afterwards filtered, washed in water, and dried in a stove for 10 h at 110–120°C. After NH_4 -Mordenite was obtained, the exchange of both ions proceeded as explained above.

2.1.5. Standard Pretreatment

Cozeolites. This stage was carried out in order to eliminate the water and nitrates present in the dry sample after the exchange. The solid was heated in O_2 at 2°C/min up to 400°C, keeping the temperature constant first for 1.5 h at 110 and 210°C and then for 8 h at 400°C. It was then cooled in O_2 at room temperature.

Pt and PtCozeolites. Mono and bimetallic solids containing Pt were calcined in O_2 at a slow heating rate of 0.5° C/min up to 350° C temperature which was kept for 2 h. The samples were then cooled in O_2 .

2.2. Catalytic Measurements

The reaction was carried out using flow equipment made up of a 12-mm ID quartz tube fixed-bed reactor. The catalyst mass was 0.5 g with a bed height of 1 cm. The typical reacting mixture was 1000 ppm of NO, 1000 ppm of CH_4 , and 1–10% O_2 , balanced at 1 atm in He (GHSV = 6500 h⁻¹). Water was introduced to the reacting stream by means of a saturator. Different concentrations were obtained by varying the working temperatures of the saturator. The catalytic activity and the composition of the reacting gases were analyzed with a Shimadzu chromatograph with two columns, one with a 5A molecular sieve and the other with chromosorb 102. The NO_x conversion was obtained from N₂ production: $C_{NO} = 2 \cdot [N_2]/[NO]^0 \cdot 100$, where $[N_2]$ is the N₂ concentration and $[NO]^0$ is the NO concentration in the feed stream. In no case was N₂O detected. The methane conversion was calculated as $C_{CH4} = ([C_{CH4}]^0 - [C_{CH4}])/[C_{CH4}]^0 \cdot 100$, with [CH₄]⁰: methane initial concentration. For comparison purposes selectivity was calculated in the same way as was defined by Li and Armor (27); that is, $\alpha = 0.5 \text{ C}_{\text{NO}}$ $[NO]^0/C_{CH4}[CH4]^0 \cdot 100$, where $[NO]^0$ and $[CH_4]^0$ are the inlet concentrations and the value 0.5 is the stochiometric ratio of methane to nitric oxide (2 molecules of nitric oxide react with 1 molecule of methane).

The calcination treatment was performed *in situ* as described in Section 2.1 catalyst preparation.

2.3. Microbalance Experiments

A Cahn microbalance (C-2000 Model) was used in the flow mode. Weight changes with time in He or NO(5%)He mixture were recordered at various temperatures.

Before adsorption, mono and bimetallic solids were calcined *in situ* as was described before and reduced with H_2 at 350°C as needed. The adsorption of the original zeolitic supports (without exchanged cations) was also measured. The weights recorded were in the presence of the ambient gas atmospheres and corrected by buoyancy.

2.4. XPS Experiments

XPS data were obtained in a Shimadzu ESCA-750 spectrometer equipped with a Mg anode (MgK = 1253.6 eV). The signal was accumulated and processed using an ESCAPAC 760 computer system. The curve-fitting processing was made using Gaussian Lorentzian component wave-forms. The (Co/Si)_s atomic ratios were calculated using the area under the Co(2p) and Si(2p) peaks. The Scofield photo-ionization cross sections, the mean free paths of the electrons, and the instrumental function were supplied by the ESCA manufacturer. The B.E. of Si(2p) was taken as a reference and measured for each support. The resulting values were 102.9 (2.5) eV for NaMordenite; 102.8 (2.4) eV for K-Ferrierite, and 103.0 (2.2) eV for NaZSM-5.

The calcined samples were subjected to the standard pretreatment and dehydration in the high vacuum chamber (slowly heated at 5°C/min up to 150°C and then up to 350° C) to eliminate the water from the solid. Afterwards, the sample was measured at room temperature. It was then reduced for 1 h with H₂ in the pretreatment chamber attached to the analysis chamber, so that the solid was not in contact with the atmosphere. Following the catalytic evaluation, the catalysts were also analyzed after the dehydration treatment in the analysis chamber described above.

2.5. TPR Experiments

Temperature-programmed reduction experiments were performed in flow equipment in a TCD detector; 0.1 g of solid was employed and 5% H₂/Ar was used as the reducing gas. The heating rate for these experiments was 10°C/min from room temperature up to 800°C and this was kept constant for 30 min. All samples were calcined according to the standard pretreatment, prior to each experiment.

2.6. FTIR Experiments

Spectra were obtained with an FTIR Shimadzu DR-8001 instrument, accumulating 2000 spectra with a spectral resolution of 4 cm⁻¹. A cell with KBr windows was used which allowed treatment *in situ*. The pellets were self-supported $(7-10 \text{ mg/cm}^2)$. The measurements were performed at room temperature in a vacuum.

3. RESULTS

3.1. Catalytic Results

In agreement with results obtained by other authors, $Co_{2.0}Mor$ was active for the SCR of NO_x with CH_4 (5,8). In fact, $Co_{2.0}Mor 43\%$ of B.E.C. (base exchange capacity) presents a maximum NO to N_2 conversion of 30% at 450°C, the selectivity index at this temperature being 22.5 (Fig. 1). When the sample was reduced at 350°C for 1 h with H_2 , a decrease of the NO conversion was observed. After treatment in O_2 overnight at 400°C, PtMor presented only 13% of NO conversion at 500°C with a very low selectivity, while the reduced monometallic samples were totally inactive to reduce NO.

The incorporation of 0.39 wt% of Pt (1.7% of B.E.C.) increases the initial activity of the oxidized $Co_{2.0}$ Mor, but after various reaction cycles the NO to N₂ conversion stabilized at values close to those of $Co_{2.0}$ Mor at temperatures below 450°C. At higher temperatures, the NO conversion on Pt_{0.5}Co_{2.0}Mor was almost twice as high as that on $Co_{2.0}$ Mor. Selectivities were comparable (Fig. 1).

When the $Pt_{0.5}Co_{2.0}Mor$ was reduced in the same way as $Co_{2.0}Mor$, the result obtained was quite different. In effect, at temperatures lower than 450°C, the NO to N₂ conversion followed the same trend as oxidized $Co_{2.0}Mor$





FIG. 1. Pretreatment effect over ion-exchanged zeolites: \bullet , \bigcirc Pt_{0.5}Co_{2.0}Mor; \triangle , \blacktriangle Co_{2.0}Mor; \bigtriangledown , \checkmark Pt_{0.5}Mor. Solid symbols: reduced samples at 350°C, 1 h with H₂ after calcination. Open symbols: calcined samples. Reaction conditions: GHSV, 6500 h⁻¹; NO, 1000 ppm; CH₄, 1000 ppm; O₂, 2% balance to one atmosphere with He.

and $Pt_{0.5}Co_{2.0}Mor$ but when the temperature was increased, the NO conversion reached 80% at 500°C and dropped to 60% at 550°C (Fig. 1).

The results obtained suggest that, after being reduced at 350° C, Pt has a promoting effect on the Co_{2.0}Mor activity. In order to determine the influence of the Pt loading on such an effect, bimetallic samples with different platinum charges were analyzed. The greater NO to N₂ conversion was obtained for a Pt content of 0.5 wt%. When the Pt content increased, the activity for CH₄ with O₂ combustion was prevalent.

The dependence of the catalytic activity on the GHSV for the $Pt_{0.5}Co_{2.0}Mor$ at 500°C was studied. As the GHSV increased from 6500 h⁻¹ to 30,000 h⁻¹, the NO to N₂ conversion underwent a decrease of about 40% but the conversion at this higher space velocity was comparable to the best cobalt-exchanged zeolite reported by Armor (6, 8, 10) under similar reaction conditions. However, in this sample the cobalt loading was higher than in the bimetallic Mordenite, viz. 4.6 wt% of Co, which gives a Co/Al = 0.76 in the Co-Ferrierite (8) against 2.87% of Co with Co/Al = 0.21 in the $Pt_{0.5}Co_{2.0}Mor$ sample.

The effect of the CH₄ concentration on the SCR of NO_x on reduced bimetallic samples was studied at GHSV = $30,000 \text{ h}^{-1}$ over Pt_{0.5}Co_{2.0}Mor. For a CH₄/NO ratio = 3 at 91% of the NO_x to N₂ conversion was obtained at 500°C. Interestingly, the CH₄ to CO₂ conversion presented a maximum at a CH₄/NO ratio = 1 and dropped to 45% for CH₄/NO = 3.

Exploratory tests under more rigorous conditions on reduced $Pt_{0.5}Co_{2.0}Mor$ were also performed at a CH_4/NO ratio = 3, at 500°C and GHSV = $100,000 h^{-1}$. The sample presented a 60% NO to N₂ conversion for 2% of O₂ in the feed-stream but such conversion dropped to 20% when the oxygen was increased to 10%.

During combustion, large amounts of water vapor are produced; consequently, an important point is to elucidate the effect of water vapor in the feed stream over the activity and selectivity of the bimetallic samples for the SCR of NO_x . Li *et al.* (25) have reported the reversible inhibition caused by water on the NO conversion over Cozeolites. In order to investigate the role of Pt in the said process, the following experiment was conducted over Co_{2.0}Mor and Pt_{0.5}Co_{2.0}Mor. A catalytic test was performed over Co_{2.0}Mor, starting with a dry mixture of 1000 ppm of NO and CH₄ with 2% of O₂ at 450°C. Then, various levels of water vapor were added to the feed stream until the NO to N_2 conversion dropped to zero. Under the same condition the bimetallic sample was then tested, but at 500°C (both temperatures correspond to the maximum NO_x conversions obtained for each sample). Results obtained with 2% of water and final stage percentages are summarized in Table 2.

Upon the addition of 2% water in the feed, the nitric oxide conversion decreased 23% over the bimetallic mordenite, while in CoMordenite a decrease of 40% was observed. When the water was removed from the feed stream, activity and selectivity were almost totally recovered in both catalysts. For the water level corresponding to the final stage, CoPtMordenite showed a 32% NO to N₂ conversion which remained constant after several hours of reaction. When the water was removed from the feed stream, activity and selectivity were totally recovered, whereas in Co_{2.0}Mor only 67% of the initial NO to N₂ conversion was obtained. This suggested that some irreversible damage had occurred in the monometallic samples. At higher GHSV the same trend

TABLE 2

Effect of Water Addition on NO and CH₄ Conversion^a

Catalysts ^b	$\underset{h^{-1}}{\text{GHSV}}$	Water %	C _{NO} (%)			C _{CH4} (%)		
			Dry	Wet	Dry ^c	Dry	Wet	Dry
Co _{2.0} Mor	6500	2 10	30 30	18 0	28 20	60 70	24 40	60 50
	30000	2	17	2	14	19	10	19
Pt _{0.5} Co _{2.0} Mor	6500	2 10	80 80	60 32	76 78	92 100	80 70	100 90
	30000	2 10	46 46	36 10	46 25	62 62	45 35	53 50

^a Reaction conditions: NO, 1000 ppm; CH₄, 1000 ppm; O₂, 2%. Temperature 450°C and 500°C for mono- and bimetallic samples, respectively. ^b Monometallic samples were calcined by standard pretreatment. Bi-

metallic solids were reduced after standard calcination.

^c After removing water of the feed stream.

TABLE 3

 $TOF \cdot 10^4 (s^{-1})$ 350°C 500°C d d Catalysts^b Co/Al Co/Pt С с α^{e} Ref. Pt_{0.5}Co_{2.0}Mor 0.21 1.91 1.94 13.0 24.3 12.6 40 This work Co_{2.0}Mor 0.21 0.28 0.69 22.5 0.60 ٤٢ Pt_{0.5}Co_{2.0}HMor 0.14 20.00.63 14 13.34 31 ۷. Pt0.5Co2.0ZSM-5 0.18 9.0 0.85 0.16 4.33 3.90 20.5 Co20ZSM-5 0.20 0.51 2.77 14.5 Pt0.5Co2.0Fer 0.19 10.6 0.61 0.56 16.5 15.0 50 ... " 30 Co_{2.0}Fer 0.14 1.3 4.0CoZSM5(11)-106 0.53 4.4 22 $(27)^{f}$ CoFer(8)-74 0.37 9.5 47 (27)79 CoFer(8)-40 0.20 6.0 (27)

Turnover Frequencies of Pt_xCo_yzeolites for NO_x Reduction^a

^{*a*} Reaction conditions: NO, 1000 ppm; CH₄, 1000 ppm; O₂, 2%; GHSV between 30,000 h⁻¹ and 100,000 h⁻¹ to keep C_{NO} below 30% (42).

^bMonometallic samples were calcined by standard pretreatment. Bimetallic solids were reduced after standard calcination.

^c TOF: Number of NO molecules converted per Co per second.

^d TOF: Number of NO molecules converted per (Co + Pt) per second.

^e Selectivity index: calculated at 500°C (see Experimental)

^f Reaction conditions: GHSV, 30,000 h⁻¹; NO, 1610 ppm; CH₄, 1015 ppm; and O₂, 2.5%.

was observed, but with a more severe decrease of No conversion on monometallic samples (Table 2).

The results obtained with the reduced $Pt_{0.5}Co_{2.0}Mor$ under different reaction conditions show that such bimetallic solids are very promising catalysts for the SCR of NO_x with methane. Thus, a deeper study of some aspects of those solids was carried out. During the H₂ reduction of $Pt_{0.5}Co_{2.0}Mor$, some Brönsted acid sites (26) may be formed; for that reason the effect of acid sties on the bimetallic solid was explored. A sample was prepared from the ammonia form of the mordenite. In this case the solid had a high concentration of Brønsted acid sites. The specific activity of cobalt, however, was not affected (Table 3).

In order to determine whether the promoting effect of Pt on the $Co_{2.0}$ Mor activity needs the intimate contact of cations, or if it is only a consequence of the presence of the metallic Pt, the following experiment was conducted: a mechanical mixture of both calcined monometallic solids was prepared so as to obtain a sample with the same loading as the bimetallic ones. The mixture was reduced at 350°C for 1 h in H₂ flow and then catalytically evaluated under the same conditions of the Pt_{0.5}Co_{2.0}Mor. The results obtained are shown in Fig. 2. Note that the maximum NO conversion is lower than 20%, while a 100% CH₄ conversion was obtained at 500°C. This suggested that an intimate contact of the active sites in the mordenite channel is necessary to obtain the desired effect.

To further investigate this effect, bimetallic samples were prepared on different zeolites, viz. ZSM-5, ferrierite and Y-zeolite, and catalytically evaluated after reduction at 350° C for 1 h in H₂ flow. Figure 3a shows the NO to N₂ conversion for the different bimetallic zeolites structure. In Fig. 3b the monometallic ones were included for comparison purposes. The NO to N₂ conversion of Cozeolites showed the same trend previously reported by Armor (10).



FIG. 2. Selective reduction of NO with CH₄ on reduced CoMor and PtMor mechanical mixture \blacksquare , \square and Pt_{0.5}Co_{2.0}Mor \bullet , \bigcirc . Open symbols: CH₄ to CO₂ conversion. Solid symbols: NO to N₂ conversion. Reaction conditions as in Fig. 1.



FIG. 3. Support effect on NO to N₂ conversion of mono and bimetallic samples: (a) reduced $Pt_{0.5}Co_{2.0}Fer \lor$; $Pt_{0.5}Co_{2.0}Mor \blacksquare$; $Pt_{0.5}Co_{2.0}ZSM-5 \oplus$; $Pt_{0.5}Co_{2.0}Y \blacktriangle$. (b) Calcined $Co_{2.0}Fer \lor$; $Co_{2.0}Mor \blacksquare$; $Co_{2.0}ZSM-5 \oplus$; $Co_{2.0}Y$. Reaction conditions as in Fig. 1.

However, when the Co loading was taken into account, they proved to be less active (Table 3). The incorporation of Pt increased the activity on the cobalt exchanged in the different zeolite structures, except for the Y-zeolite, which proved inactive for both mono and bimetallic solids. The promoting effect became evident when the solids were reduced in H_2 flow for 1 h at 350°C (Fig. 3a and Table 3).

In the search of a better understanding of the Pt promoting effect and in an attempt to elucidate the nature of the active sites, NO adsorption studies were performed and the different solids were also studied by TPR techniques and XPS. FTIR was also used to characterize the Brønsted acid sites.

3.2. NO Adsorption Results

With the purpose of studying the effect of Pt on the capability of the catalyst to adsorb NO, adsorption of such a reaction at different temperatures was measured on mono and bimetallic samples. Some of the preliminary data are shown in Table 4. The results obtained on CoMordenite and CoFerrerite are, in general, in agreement with the ones reported by Zhang et al. (28). In fact they reported a NO/Co ratio of 0.25 molecules NO_x/Co^{2+} at 250°C on CoMordenite (Si/Al = 5.25, 65% of B.E.C.) against 0.10 molecules $/Co^{2+}$ at 300° C (Si/Al = 5.9, 43%) in this work (Table 4). Interestingly, the NO adsorbed in the reduced bimetallic samples was higher than in the monometallic ones, viz. 0.53 vs 0.17 molecules NO/Co⁺² on ferrierites and 0.27 vs 0.10 on mordenite, respectively (Table 4). In the same vein Ogura and Kikuchi (20) found that the addition of precious metals-particularly Ir-to InZSM5 enhanced the abilities of the catalyst to adsorb NO and to increase the amount of NO₂ adsorbed on In sites.

3.3. XPS Results

Bimetallic solids $Pt_{0.5}Co_{2.0}Mordenite$, $Pt_{1.0}Co_{2.0}Mordenite$, $Pt_{0.5}Co_{2.0}ZSM5$, and $Pt_{0.5}Co_{2.0}Ferrierite$ and monometallic $Co_{2.0}Mordenite$ were analyzed by XPS. The measurements were performed in the binding energies region corresponding to Si(2p), Al(2p), Pt(4f), Co(2p), and C(1s).

Al(2p) was also measured in the supports, obtaining the following B.E.s: 74.5(2.0) eV in Na-Mordenite, 74.6(2.6) eV

TABLE 4

Microbalance Data for NO Adsorption at 300°C on Pt Co Zeolites^a

Samples	Pretreatment	NO cm ³ \cdot g ⁻¹	NO/Co	
Co _{2.0} Fer	Calcined ^b	0.89	0.170	
Pt _{0.5} Co _{2.0} Fer	Calcined ^b	0.041	0.006	
Pt _{0.5} Co _{2.0} Fer	Reduced ^c	3.62	0.530	
Co _{2.0} Mor	Calcined ^b	1.11	0.10	
Pt _{0.5} Co _{2.0} Mor	Calcined ^b	0	0	
Pt _{0.5} Co _{2.0} Mor	Reduced ^c	1.43	0.27	
CoMor ^d	Calcined ^e	26.9	1.67(25°C) ^f	
		6.5	0.33(200°C) ^f	
		5.0	0.25(250°C) ^f	

^{*a*} Calculated from the weight increase on NO adsorption. The values are the difference in weight after exposure to the NO/He stream and the weight of catalyst following pretreatment divided by the total Co content. The adsorption time was 60 min. The zeolites were pretreated in flowing O₂ overnight, purged with dry He for 1 h, cooled to 300°C in He flow before contacting with a stream of 5% NO in He.

- ^b See experimental.
- ^c Reduced in pure H₂ for 1 h.
- ^d Ref. (28). CoMordenite, Si/Al = 5.2, 65% B. E. C.
- ^e Dried in air at 110°C and heated in He at 500°C for 5 h.
- ^f In brackets, NO adsorption temperature.

 TABLE 5

 XPS Data of Pt and Co Zeolites

		Co2p _{3/2} energy			
Catalysts	Treatment	Co ²⁺	Co^0	Co/Si) _s ^b	
Co _{2.0} Mor	Calc. 400°C	783.1	_	0.09	
	Red. 350°C	783.4	_	0.05	
Co/SiO ₂	Calc. 400°C	781.5	_	0.22	
	Red. 350°C	—	778.2	0.08	
Pt _{1.0} Co _{2.0} Mor	Calc. 400°C	783.1	_	0.08	
	Red. 350°C	783.3	778.3	0.08	
Pt _{0.5} Co _{2.0} Mor	Calc. 400°C	783.1	_	0.08	
	Red. 350°C	783.3	_	0.05	
	Reoxid. 550°C ^c	783.8	_	0.08	
	After reaction ^d	783.2	_	0.14	
Pt _{0.5} Co _{2.0} ZSM5	Red. 350°C	783.4	_	0.06	
	After reaction	783.2	—	0.11	
Pt _{0.5} Co _{2.0} Fer	Red. 350°C	783.7		0.07	
	After reaction	783.4	—	0.12	

^{*a*} The binding energy values are referred to Si(2p): 102.9 (2.5) eV for Na-Mor; 102.8 (2.4) eV for K-Fer; 103.0 (2.2) eV for Na-ZSM-5; and 103.8 eV for SiO₂.

^b Surface Co/Si ratio calculated from XPS experimental data.

^c The reduced sample was reoxidized with pure O₂.

^{*d*} Reaction condition: GHSV, 6500 h^{-1} , NO, 1000 ppm; CH₄, 1000 ppm, O₂, 2% balanced to one atmosphere with He.

in K-Ferrierite, and 74.4 (1.9) eV in Na-ZSM-5, where the medium height width is indicated between brackets. The samples were analyzed after different treatments: (a) calcination, (b) *in situ* reduction, (c) after reduction at 350° C, reoxidation at 550° C (*ex situ*) under pure oxygen, and (d) under reaction stream for several hours (Table 5).

The Pt(4f) signal partially overlaps with that of Al(2p); consequently, it was not possible to accurately determine the signal corresponding to Pt in the bimetallic samples with 0.5 wt%. When samples with a higher content (1 wt%) were studied, binding energies of Pt^{2+} (73.1 eV) and Pt^{0} (71.9 eV) were observed on both calcined and reduced solids.

In the bimetallic solids subjected to the different treatments mentioned above, the Al(2p) B.E. was modified only at ± 0.2 eV. The Co(2p_{3/2}) B.E. is shown in Table 5, together with the Co/Si surface ratios. In all the bimetallic solids with 0.5 wt% of platinum, the only signal observed (approximately 783.2 eV) was the one assigned by several authors (29, 30) to the ions of Co⁺² located at exchange positions within the zeolitic structure. This signal was not modified either after reduction at 350°C or after reoxidation at 550°C under pure oxygen. Only in the reduced Pt_{1.0}Co_{2.0}Mor did the Co²⁺(783.3 eV) and Co⁰(778.3 eV) signals coexist. The B.E. metallic cobalt was comparable to that of Co/SiO₂. The Co/Si surface ratio increased in the solids used after reaction, thus indicating a surface enrichment of the cobalt.

3.4. TPR Results

Figures 4, 5, and 6 show the temperature-programmed reduction results for mono- and bimetallic PtCozeolites. The H₂ consumption per mol of Co and/or Pt is expressed in Table 6. The H₂ consumption indicated that approximately one molecule of H₂ is consumed per platinum ion (Table 6). This would indicate that the average oxidation state of platinum remains divalent after calcination at 350° C.

Co_{2.0}Mor presents two well-defined maxima at 425 and 750°C, respectively (Fig. 4). For temperatures lower than 600°C, the H₂ consumption per Co mol indicates that only 8% of the total cobalt is reduced in this area, while at higher temperatures, the degree of reduction reaches 35%. The 425°C peak could be assigned to a fraction of the cobalt supported as oxide on the external surface of the mordenite while the maximum at 750°C may be due to the Co²⁺ reduction at exchange position.

 $Pt_{0.5}Mor$ presents two reduction maxima at 290 and 625°C. The H₂ consumption per platinum mol was 0.51 and 0.38, respectively, for each peak (Fig. 4 and Table 6). This type of TPR profile could be attributed to the Pt exchanged at different sites in the mordenite structure.

The reduction profile of the bimetallic $Pt_{0.5}Co_{2.0}Mordenite catalysts does not correspond to the sum of its respective monometallic <math>Co_{2.0}Mor$ and $Pt_{0.5}Mor$ (Fig. 4), with maxima at 277, 456, 619, and 775°C.

In the zone of temperatures lower than 400°C, the H_2 consumption indicates that 21% of the cobalt is reduced, whereas at higher temperatures, 81% is reduced. It should be remarked that in this higher temperature region, two well-defined peaks are observed, while in Co_{2.0}M there is only one peak which started at approximately 600°C and finished at about 800°C. The increase in the reducibility of



FIG. 4. TPR profile of Co and Pt mono and bimetallic mordenite samples.

TABLE 6

Catalysts	μ moles H ₂ ^{<i>a</i>}		$H_2/(Co + Pt)^b$	H ₂ /Co ^c	
	20/400°C	400/800°C	20/800°C	20/400°C	400/800°C
Co _{2.0} Mor	_	21	0.43	_	0.43
Pt _{0.5} Mor	0.96	0.73	0.89	_	_
Pt _{0.5} Co _{2.0} Mor	11.2	40.3	1.02	0.21	0.81
Pt _{0.5} Co _{2.0} Mor used	—	35.35	0.7	—	0.73
Co _{2.0} ZSM5	0.61	21.49	0.72	0.02	0.70
Pt _{0.5} ZSM5	1.72	2.35	1.10	_	_
Pt _{0.5} Co _{2.0} ZSM5	8.5	22.9	1.03	0.24	0.75
Co _{2.0} Fer	2.3	11.74	0.6	0.10	0.50
Pt _{0.5} Fer	0.5	1.26	0.8	_	_
Pt _{0.5} Co _{2.0} Fer	18	15	1.0	0.57	0.45

Co and Pt Zeolites Reducibility from TPR Data

^{*a*} H₂ consumption per 0.1 g of sample.

^{*b*} H_2 consumption in TPR per (Co + Pt) moles.

 c H₂ consumption per Co moles (The corresponding to Pt reduction was substracted from the total H₂ consumption).

Co and the different shapes of the TPR profile (Fig. 4 and Table 6) strongly suggest a promoting effect of Pt on the reducibility of Co exchanged in mordenite.

The thermograms in Fig. 5 present the reduction peaks of Pt, Co, and PtCo exchanged in Na-ZSM-5. The Pt_{0.5}ZSM-5 monometallic sample has a broad reduction peak between 100 and 400°C with a maximum ca 200°C. The main peak appears well defined at 700°C and the reduction is completed at 800°C, reaching the signal of the base line. As in the case of Pt_{0.5}Mor the H₂ consumption suggested that the average oxidation state is Pt²⁺.

The $Co_{0.5}ZSM$ -5 reduction (Fig. 5) presents a very small signal at around 300°C while the main peak occurs at 700°C.



FIG. 5. TPR profile of Co and Pt mono and bimetallic ZSM5 samples.

Approximately, 70% of the cobalt ions are reduced in this region.

In the $Pt_{0.5}Co_{2.0}ZSM$ -5 bimetallic solid three reduction maxima are observed at 325, 570, and 700°C, respectively. The H₂ consumption per mole of (Co + Pt) is close to 1, which would indicate the complete reduction of both ions (considering as +2 the average oxidation state).

By analyzing the H₂ consumed at temperatures lower than 400°C, it could be established that 25% of the total cobalt of the solid is reduced, which means a noticeable increase of the cation reducibility in this region if compared to Co_{2.0}ZSM-5, in which only 2% of the reduced cobalt is observed. However, the average reduced cobalt at temperatures higher than 500°C (73%) is similar to that observed for the monometallic sample, but in the bimetallic sample the maxima were well defined and the peaks shifted towards lower temperatures than in the monometallic one (Fig. 5 and Table 6).

Figure 6 shows the reduction profiles for Pt, Co, and PtCo exchanged in K-Ferrierite. In Co_{2.0}Fer, similarly to the other supports, two peaks are observed at 475 and 705°C, respectively. At low temperatures only 10% is reduced while at higher values, reduction reaches 50%. In Pt_{0.5}Fer there appears a small signal at 190°C and, afterwards, a very broad peak from 300°C with a maximum at 490°C and another one close to 600°C. Throughout this temperature range the ratio of consumed H_2 per Pt was 0.8. The reducibility at temperatures lower than 400°C was 10% while at higher temperatures, it reached 68%. At low temperatures, the bimetallic solid Pt_{0.5}Co_{2.0}Ferrierite presents two reduction peaks at 235 and 330°C, respectively, differing from the other bimetallic samples, Pt_{0.5}Co_{2.0}Mordenite and Pt_{0.5}Co_{2.0}ZSM5, which show a single signal in this region. In this zone, 57% of the cobalt present is reduced,



FIG. 6. TPR profile of Co and Pt mono and bimetallic Ferrierite samples.

thus increasing the reducibility due to the presence of platinum. At higher temperatures (from 400 to 700°C) a very broad signal is observed, as well as a small peak with a maximum at 690°C. H₂/Co was 0.45, the same as the monometallic samples. The H₂ consumption per mol of Co plus platinum is close to the unit, which would indicate that in the whole range both ions, Pt and Co, are completely reduced.

The reducibility of the sample used in the reaction was also studied by temperature-programmed reduction. In Fig. 7, the TPR profiles of the fresh and used $Pt_{0.5}Co_{2.0}Mordenite$ samples are compared. Both profiles are different.



FIG. 7. TPR profile of $Pt_{0.5}Co_{2.0}Mor$: (A) reduced fresh and (B) after 50 h under reaction at 500°C. Reaction conditions as in Fig. 1.

The used sample did not present reducibility at low temperatures and started to reduce from 400°C, producing a peak with a maximum approximately at 700°C. The H₂ consumption measured by moles of (Co + Pt) was 0.7 (Table 6).

3.5. FTIR Results

As pointed out before, the reduction of the samples may produce some Brønsted acid sites. In order to clarify this hypothesis, a series of experiments were carried out employing FTIR. In Fig. 8A, the region of the acidic OH (3600 cm⁻¹) of calcined monometallic (8 h in O₂ flow at 400°C) mordenites is compared to that of the bimetallic ones. The sample prepared over NH₄Mordenite is also included.

It can be observed that all solids present a band at 3600 cm^{-1} with a better definition in the case of $Pt_{0.5}Co_{2.0}$ Mordenite (Fig. 8A.a). The presence of adsorbed H₂O (band at 1630 cm^{-1}) is observed in all the samples, probably due to the fact that the O₂ stream used during calcination may contain water vapor.

When the samples reduced in H₂ stream at 350°C for 1 h are compared, an increase of the signals corresponding to the acidic OH is observed (Figs. 8A and B). However, the signal corresponding to the bimetallic samples is less defined, probably due to the fact that the water which remains absorbed in the sample after being evacuated for 1 h is higher than in monometallic samples (greater extension of the reduction in the bimetallic samples compared with the monometallic) (Figs. 8A.a and 8B.a).

In the case of the $Pt_{0.5}Co_{2.0}HMor$, the band at 3600 cm⁻¹ of the calcined and reduced samples were comparable; this probably is due to the smaller contribution of the Brønsted sites generated by reduction, compared with the acid sites already in existence of H-Mordenite (Figs. 8A.b and B.b).

4. DISCUSSION

The results appearing in Figs. 3a and b and Table 3 clearly show the promoting effect of the Pt incorporated to Cozeolites on the SCR of NO_x with CH₄. This promoting effect is a function of the zeolite type and, for a given zeolite, of the pretreatment of the catalysts and Pt loading (Fig. 1). The reduction with H₂ at 350°C of bimetallic mordenite (Co/Al = 0.21) yielded a solid which converts 91% of NO to N₂ at GHSV of 30,000 h⁻¹ and 60% at 100,000 h⁻¹ with a CH₄/NO ratio of 3 at 500°C and 2% of oxygen on the feed stream. PtCoFerrierite (Co/Al = 0.19) gave 50% of NO conversion at GHSV = 30,000 h⁻¹ at 500°C but with NO/CH₄ = 1 and 2% O₂. On the other hand, the catalysts remained stable for a long while (over 100 h) under reaction conditions at the above temperature.

At this point, a comparison of the bimetallic zeolites against the most active Co monometallic zeolites could



FIG. 8. Effect of cation exchange on OH development on (A) calcined samples, (B) reduced samples: (a) $Pt_{0.5}Co_{2.0}Mor$; (b) $Pt_{0.5}Co_{2.0}HMor$; (c) $Pt_{0.5}Mor$; (d) $Co_{2.0}Mor$.

be relevant. Li and Armor (8, 27) reported a variety of cobalt zeolites that were evaluated for the above reaction at GHSV = 30,000 h⁻¹, for a CH₄/NO ratio of 0.63 and 2.5% of O₂. They found that the NO to N₂ conversion over CoFerrierite increases with the level of Co^{2+} at lower cobalt loadings (viz. Co/Al = 0.2–0.37) but remains essentially constant at higher loadings (viz. Co/Al = 0.37–0.50) while the TOF increases with the cobalt loading at low levels of Co²⁺, but it decreases at higher levels. On CoZSM-5 the activity also depends on the cobalt level in zeolites. The TOF on these samples was constant at Co/Al < 0.33 but was much lower on over-exchanged CoZSM-5.

Taking into account the results discussed before, a comparison with samples with similar Co/Al ratios seems appropriate. The said authors reported that CoFerrierite with Co/Al = 0.37 gives 47% of NO to N₂ conversion at 500°C (TOF = $9.5 \times 10^{-4} \text{ s}^{-1}$, Table 3) and a selectivity index $\alpha = 47$ (27). The same ferrierite but with Co/Al = 0.20 gives only 17% of NO to N₂ conversion (TOF = $6 \times 10^{-4} \text{ s}^{-1}$, Table 3) and a selectivity index $\alpha = 79$, while CoZSM-5 with Co/Al = 0.53 gives 28% of NO to N₂ conversion at the same temperature (33% of conversion at 450°C) and a selectivity index $\alpha = 22$ (TOF = 4.4×10^{-4} , Table 3). Armor (8) reported that CoMordenite Co/Al = 0.4 gives 24% of conversion at 500°C. Comparable results were reported by Witzel *et al.* (31) and Lukyanov *et al.* (32) under somewhat different reaction conditions. The former reported that at GHSV = 9000 h⁻¹, CH₄/NO = 4 and 10% of O₂ that both CoFerrierite (Co/Al = 0.39) and CoZSM-5 (Co/Al = 0.49) give 100% of NO to N₂ conversion at 500°C with a selectivity index of 1. The latter reported that at GHSV = 45,000 h⁻¹ CH₄/NO = 1.33 CoZSM-5 (Co/Al = 0.49) gives 40% of NO conversion at 500°C with a selectivity index $\alpha = 33$.

Results obtained with the monometallic zeolites in this work are in a similar vein with the ones discussed before (Fig. 3b) but the bimetallic solids present a better activity for the SCR of NO with comparable selectivity (Table 3).

Let us now focus our attention on the behavior of Pt monometallic zeolites. Results obtained with reduced samples were in agreement with those previously reported by Burch and Scire (11) and Li and Armor (7), who found that Pt-exchanged ZSM-5 was completely unselective towards the nitric oxide reaction with methane in the presence of oxygen. In contrast, in the absence of oxygen PtZSM-5 converts 93% of NO to N₂ at 450°C (11). With other

hydrocarbons like ethane, propene, and propane, PtZSM-5, as well as platinum, on other supports (calcined or reduced catalysts) have been reported to be active in the SCR of NO_x at lower temperatures (33–36).

The results discussed before on monometallic Co and Pt zeolites suggest that the catalytic behavior observed in the bimetallic samples is not a consequence of the sum of the individual effects of either cation. Besides, the lower conversion of NO to N₂ over the mechanical mixture of both monometallic solids, compared with the bimetallic samples (Fig. 3), indicates that the cooperative effect of platinum over Co-exchanged zeolite structures is different from the one reported by Inaba et al. (35), in the case of Pt and alumina for the SCR of NO_x with propane. In fact, those authors found that the activity of the mixture of Pt/SiO₂ and Al_2O_3 (when the grain size of the mixture was 80–100 mesh) was similar to that of Pt/Al₂O₃. They attributed such cooperative effect to the spillover or gas-phase transfer of some reaction intermediates from platinum to alumina or vice versa.

Several systems which present the cooperative effect by combination by two different catalysts mixed together mechanically or physically have been reviewed by Hamada (37). One of these systems which could be somehow related to the bimetallic CoPtzeolites is the combination of Pd and H-ZSM-5, studied by Loughran and Resasco (12). They found that when H-ZSM5 was mechanically mixed with Pd/SiO₂, the resulting activity for the SCR of NO_x with CH₄ was much lower than that of the palladium directly supported on H-ZSM-5. By contrast, when SO_4^{2-}/ZrO_2 was used in the mechanical mix with Pd/SiO₂, the resulting activity exhibited about the same conversion level as that observed on the Pd directly supported on SO_4^{2-}/ZnO_2 catalysts. These authors assumed that such different behavior was due to the limitation of transfer of reaction intermediates from palladium to the acid sites or vice versa through zeolite cages. In the bimetallic CoPtzeolites, it would seem that for the cooperative effect to occur, both cations need to be in intimate contact inside the channel or on the surface of the mordenite. This could be due either to an effect similar to the one described above (12) or to the fact that such solids are uniform catalysts containing two or more catalytic species, where their role is sometimes difficult to differentiate (Hamada classification (37)). A case in point is the Pd/Co/H-ZSM5 system reported by Ogura et al. (22). The possible formation of alloy or intermetallic compounds between Pt and Co cannot be ruled out.

Results derived from the XPS and TPR studies of the mono and bimetallic samples may shed light on the hypotheses discussed before. XPS only detected Co^{2+} located at exchange position in solids that were calcined, reduced, reoxidized, or on reaction stream at 550°C for long periods (Table 5). No significant changes in the BE of $Co(2p_{3/2})$ were detected, comparing the three zeolites studied, viz. morden-

ite, ZSM-5, and ferrierite. The signal corresponding to the binding energy of supported cobalt oxide (B.E. 781.5 eV) was detected neither in calcined samples (O_2 treatment at 450°C) nor in reoxidized ones (O_2 treatment at 550°C after reduction at 350°C), probably due to the low amount of such species. In fact, the TPR results (Table 6) show that only a 0.6% of Co was reduced at temperatures lower than 400°C in PtCoMordenite (vide infra). Consecuently the possibility of Co₃O₄ particles formation cannot enterely be ruled out. No Co⁰ signal was detected after reduction at 350°C in samples with low Pt loading, but when samples with 1% of Pt were analyzed after reduction, the Co° signal was detected in the XPS spectra. The B.E. of Co° in PtCoMor is comparable to that of Co°/celite. This somehow differs from the results reported by Zsoldos et al. (38) who, in their studies of Pt_(7.0)Co_(2.0)YZeolites, found a shift of approximately 0.7 eV in the Co²⁺ B.E. between the mono and bimetallic samples. They attributed this effect to the CoPt interaction and to the subsequent formation of bimetallic particles. A similar positive B.E. shift for $Co(2p_{3/2})$ was observed in CoPt₃ intermetallic (39). In the PtCozeolites used in this study, this possibility cannot be totally ruled out due to the low content of surface Pt of the samples (surface Co/Pt > 20and bulk Co/Pt = 5 to 24). Further evidence of such hypothesis could be found in the results reported by Boix *et al.* (40) who, by DRX, detected CoPt3 particles on PtCoMordenite only for bulk Co/Pt ratios lower than 0.5.

The promoting effect of Pt on the Co reducibility was confirmed through TPR studies. Despite the different zeolitic structures, from the thermograms in Figs. 4, 5, and 6 and Table 6, it is clear that the behavior of the bimetallic samples does not correspond to the sum of each monometallic one. The H₂/Co ratio in the low temperature range notably increases if compared with Pt and Co zeolite (Table 6). Besides, in the TPR profile two sharp maxima appear, at 600 and 650°C in the Pt_{0.5}Co_{2.0}Mor and Pt_{0.5}Co_{2.0}ZSM-5, respectively (Figs. 4 and 5). The above behavior could be explained in terms of the mechanism of the platinum-promoting effect suggested by Lu *et al.* (41) on CoPtYzeolite. In that mechanism, topographically located cobalt ions can be reduced by the hydrogen atoms generated by the platinum which has been reduced at the commencement of the reduction. Cobalt could also be reduced in $PtCo_xO_y$ oxides. Both effects seem possible in PtCoMordenite and PtCoZSM-5. In fact, the increase in the reducibility of cobalt at low temperatures could be attributed to the formation of such types of oxides located inside of channels or in the outer surface of the zeolites, whereas the reduction at high temperatures would correspond to the catalytic action of platinum upon the nearby Co²⁺ cations (Figs. 4 and 5). PtCoFerrierite showed the same trend but now it seems likely that the catalytic action of Pt^0 in the reducibility of Co^{2+} at high temperatures is less evident (Fig. 6 and Table 6). A more detailed study,

however, is necessary before a stronger assumption is put forward.

It should be noted that Boix *et al.* (40) found that the bimetallic species resulting from the reduction of $PtCo_xO_y$ were segregated after reoxidation at 500°C. They explained such behavior, assuming that after reduction of the $PtCo_xO_y$ clusters of highly dispersed Pt° and Co° were obtained.

Despite the oxygen excess, the Co° and Pt° formed during reduction remained under reaction conditions (Fig. 7 and Table 6). However, as suggested by the Co surface enrichment (Table 5) and the change of the TPR profile (compare Figs. 4 and 7) in used samples, some reorganization of the species may have occurred under reaction.

This complex system yields very active and selective catalysts for the SCR of NO_x with methane. Several concurring causes could be responsible for such effect. NO₂ has been proposed by various authors as an important intermediate in the reaction scheme (8, 10, 32, 42, 43). Bifunctional mechanisms have been formulated for Ga/H-ZSM5 and In/ H-ZSM5 by Kikuchi and Yogo (44), where the authors suggested that the NO + $1/2O_2 \rightarrow NO_2$ reaction occurred on the zeolitic acid sites. If at this point a comparison is made with PtCo zeolites it seems likely that the acid sites generated during reduction do not play a central role. In fact, the TOF of PtCoMordenite and PtCoHMordenite were comparable (Table 3), despite the bigger amount of Brönsted sites in the latter (Fig. 8).

A similar bifunctional mechanism was proposed by Nishizaka and Misono (13) for the Pd/H-ZSM-5 and Pd/ Ce-ZSM-5. They also confirmed that NO oxidation is the first important step for the Ce-ZSM-5 catalyzed the SCR of NO with propene (45). Besides, they found that a mechanical mixture of such material with NO oxidation catalysts like Mn₂O₃ or CeO₂ gives a solid with higher NO reduction activity than the Ce-ZSM-5 in the lower temperature region (46). The same results were reported by Iwamoto et al. (13, 24) for PtZSM5, combined with different metal ZSM5 zeolites through the IAR (intermediate addition of reductant) approach. This could also be a suitable explanation for the promoting effect of platinum in PtCozeolites due to the high activity of Pt for NO oxidation, as was proposed by Kikuchi et al. for SCR of NO_x with CH_4 under wet conditions over PtIn/H-ZSM5. However, such a promoting effect in the bimetallic samples was more evident at high reaction temperatures, viz. higher than 450°C (Fig. 3) (47). Consequently, Pt may play another role besides the one discussed above. This additional role could be to enhance the ability of the catalyst to adsorb NO as suggested by the results obtained in the NO adsorption on the reduced bimetallic samples (Table 4). This also could increase the amount of NO_2 adsorbed on Co^{2+} sites as was found by Ogura *et al.* (20) when precious metals were loaded to In/H-ZSM-5.

Contrary to this, a synergetic effect can occur among the different sites in intimate contact in an adequate zeolite structure. In this scheme Pt may help toward activating CH₄,—which takes place at temperatures higher than 400° C (11)—to react then with the NO₂ adsorbed on Co²⁺ (48) and form CH_3 radicals (36, 49). The protonic acid sites may also favor the NO₂ formation. As the Pt loading increases, a larger fraction of platinum may reside outside the zeolite channel and the oxidation of CH₄ with oxygen prevails. This CH₄ activation is consistent with the kinetic isotope studies of Cowan et al. (50) that prove that the cleavage of the C-H bond is the rate-determining step in the SCR of NO. The Pt loading increase is also in agreement with results reported by Loghran and Resasco (12) for Pd/HZSM-5 catalyst. Ogura et al. (20) for a different catalyst, viz. Pd/Co/HZSM-5, also explained the promoting effect of Pd in such solids, assuming that highly dispersed Pd^{+2} catalyzed the reaction between NO₂ and CH₄, while Co⁺² would act as the NO oxidation catalyst. Research in progress may help to elucidate whether any of the previous proposals, so far speculative, are feasible.

Finally it is necessary to single out for comment one of the points mentioned in the Introduction regarding the stability of the catalysts under wet conditions. The results obtained on PtCoMordenite (Table 2) show a positive effect of Pt on the water resistance of Cozeolite. However, the results obtained on CoMor appear to be somewhat different from the ones reported by Li *et al.* (25) for comparable catalysts. A deeper study of the water and SO₂ effect is necessary to arrive at final conclusions on the stability of the PtCozeolites under real reaction conditions.

5. CONCLUSIONS

—Pt promotes the NO to N_2 conversion on SCR with CH₄ over Cozeolites. The catalysts obtained proved to be stable under dry and wet conditions in the temperature ranges studied. (Fig. 3, Tables 2 and 3).

—The above promoting effect was a function of the zeolite type, of the pretreatment of the catalyst, and of the platinum loading. Treatment of the solids in H₂ flow at 350°C for 1 h with about 0.5 wt% platinum yielded a catalyst which gives 60% of NO conversion at 100,000 h⁻¹ at 500°C with an CH₄/NO ratio of 3 and 2% O₂.

—The intrinsic activity of Pt promoting catalysts depends on the zeolite matrix. The order of activity expressed as turnover frequency (Table 3) was: $Pt_{0.5}Co_{2.0}Fer > Pt_{0.5}Co_{2.0}Mor > Pt_{0.5}Co_{2.0}ZSM-5$.

—XPS, TPR, and FTIR results show that Co^{2+} , Pt^{2+} , and probably some $PtCo_xO_y$ oxides were present in the calcined samples. After reduction in H₂ at 350°C, in addition to the cations in the exchange position, Co° , Pt° , and some acid sites were developed. Such species remain under reaction conditions but some reorganization would occur (Figs. 4 and 7 and Tables 5–6).

—In order to obtain a suitable catalyst for the SCR of NO_x , the active species must be present in intimate contact. The zeolite matrix also plays an important role, viz.

the CoYzeolite was inactive for the said reaction and it remained so after the platinum was incorporated (Figs. 2, 3a and b).

—The highest activity and selectivity of the PtCozeolite could be explained as a synergetic effect (cooperative effect) of the above species inside the zeolite channels, which enhances the ability of the catalysts to adsorb NO (Table 4).

—The results obtained with the highest levels of water in the feed stream suggest that Pt has positive effect on the water resistance of the Cozeolites. However, more studies on such a system are necessary to conclude that they are suitable catalysts under real reaction conditions. Results obtained so far are very promising.

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