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Effect of Pt on the water resistance of Co-zeolites upon the SCR of NO_x with CH_4

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Abstract

The objective of this work was to study the promotional effect of Pt on Co-zeolite (viz. mordenite, ferrierite, ZSM-5 and Y-zeolite) and Co/Al_2O_3 on the selective catalytic reduction (SCR) of NO_x with CH_4 under dry and wet reaction stream. After being reduced in H_2 at 350°C, the PtCo bimetallic zeolites showed higher NO to N_2 conversion and selectivity than the monometallic samples, as well as a combination of the latter samples such as mechanical mixtures or two-stage catalysts. After the same pretreatment, under wet reaction stream, the bimetallic samples were also more active. Among the other catalysts studied with 5% of water in the feed, ($NO = CH_4 = 1000$ ppm, $O_2 = 2\%$), the NO conversion dropped to zero over $Co_{2.0}$Mor at 500°C and GHSV = 30,000 h^{-1}, whereas it is 20% in $Pt_{0.5}Co_{2.0}$Mor. In $Pt/Co/Al_2O_3$ the NO_x conversion dropped below 5% with only 2% of water under the same reaction conditions. The specific activity given as molecules of NO converted per total metal atom per second were $16.5 \times 10^{-4}\,s^{-1}$ for $Pt_{0.5}Co_{2.0}$Fer, $13 \times 10^{-4}\,s^{-1}$ for $Pt_{0.5}Co_{2.0}$Mor, $4.33 \times 10^{-4}\,s^{-1}$ for $Pt_{0.5}Co_{2.0}$ZSM-5 and $0.5 \times 10^{-4}\,s^{-1}$ for $Pt/Co/Al_2O_3$. The Y-zeolite-based samples were inactive in both mono and bimetallic samples. The species initially present in the solid were Pt° and Co°, together with Co^{2+} and Pt^{2+} at exchange positions. Co° seems not to participate as an active site in the SCR of NO_x. Those species remained after the reaction but some reorganization occurred. A synergetic effect among the different species that enhances both the NO to NO_2 reaction, the activation of CH_4 and also the ability of the catalyst to adsorb NO, could be responsible for the high activity and selectivity of the bimetallic zeolites. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: Selective catalytic reduction; No_x; Water resistance; Zeolites; PtCo-zeolites; $Pt/Co/Al_2O_3$

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1. Introduction

The use of CH_4 as reducing agent for the selective catalytic reduction of NO_x 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 producing NO_x during the combustion process.

Recently, several active catalysts for the SCR of NO_x with CH_4 have been reviewed by Armor [1], who concluded that Co in Co-ZSM-5 and Co-Ferrierite appear to be more reactive than other transition metal ions. However, none of these catalysts are sufficiently effective in wet atmospheres. The author estimated that Co-Ferrierite is about a factor of four too low in activity for commercial applications in stationary engines.

Ga- and In-loaded H-ZSM-5 catalysts are also active for the above reaction [2] but they are also significantly poisoned by water vapor and SO_2 (unfortunately present in the exhaust gas stream). Noble-metal

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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 [3] have a high selectivity in the absence of oxygen but when 2% of O_2 is added to the feed, platinum is not selective, the NO to N_2 conversion being only 3% with 25% of N_2O. Under such conditions, Rh-ZSM-5 presents 25% of NO conversion with approximately 10% of NO_2 at 450°C.

PdH-ZSM-5 was first reported by Misono et al. [4] as an active catalyst for the reduction of NO with CH_4. Since then, Pd-based catalysts supported on various solid acids have been employed with the same purpose [5,6]. In their study of the SCR of NO_x with CH_4 over palladium-exchanged mordenite, Descorme et al. [7] interestingly found that the activity is increased by the addition of 10% of water in the feed stream (2000 vpm NO, 1000 vpm CH_4, 1000 vpm O_2 in the GHSV = 30,000 h^{-1}). They attributed such behavior to a migration of Pd ions from hidden to accessible sites. However, the highest NO to N_2 conversion of those solids reported so far is only 25% at 450°C.

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. One of the ideas that many researchers have explored to achieve the above objective is to create catalysts of high activity and selectivity by the combination of catalytic sites for NO oxidation and NO reduction [8]. For example, interesting results were reported by Kikuchi and co-workers [6,9,10,11], who found that precious metals (Pt, Rh or Ir) added to In/H-ZSM-5 improve the NO conversion in the selective reduction with methane under wet conditions. They suggested that the bifunctional catalysis of such solids is remarkably facilitated by the co-existence of the active sites in the pores of the zeolite, what these authors call ‘intrapore catalysis’. Ogura et al. [12] also found 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. Recently, Yan et al. [13] reported a synergetic effect when Co/Al_2O_3 was physically mixed with H-ZSM-5. In fact, they found that the NO to N_2 conversion with CH_4 over such physical mixture was twice as high as that expected if the components acted independently.

Another interesting catalytic process also based on the concept of cooperative (bifunctional) effect was found by Iwamoto et al. [14,15]. They reported that the intermediate addition of ethane (IAR) to a NO + O_2 stream in a twin reactor system with Pt-ZSM-5 in the first reactor and different monometallic ZSM-5 in the second, increases the effectiveness of the monometallic zeolites.

We also found that Pt added to C-zeolites (viz. mordenite, ZSM-5 and ferrierite) promoted the NO to N_2 conversion with CH_4 [16,17]. In the present work, a more detailed study of the effect of Pt on the water resistance of Co-zeolites is presented. The role of the Pt–Co interaction and the effect of the support on that interaction are also investigated. An attempt is made at elucidating the species present in the bimetallic zeolites.

2. Experimental

2.1. Catalysts preparation

By Pt and Co ionic exchange, catalysts were prepared on the following zeolitic matrixes: Na-Mordenite $[Na_7(AlO_2)_7(SiO_2)_{41}]$, Na-ZSM-5 $[Na_9\cdot(AlO_2)_9(SiO_2)_8$, K-Ferrierite $[(Na,k)_{3,7}(AlO_2)_{3,7}\cdot(SiO_2)_{32,3}]$ and Na-Y$[Na_{56}(AlO_2)_{56}(SiO_2)_{136}]$.

Mono and bimetallic solids were obtained following the previously described techniques [17].

The alumina-based samples were prepared by the wet impregnation method using $Pt(NH_3)_4(NO_3)_2$ for Pt/Al_2O_3 and $Co(NO_3)_2$ for Co/Al_2O_3. The $Pt/Co/Al_2O_3$ catalyst was prepared by successive impregnation.

The mechanical mixture was prepared from previously calcined monometallic solids, keeping the Co/Pt ratio equal to that of the bimetallic samples.

All zeolite-based catalysts were pretreated in O_2 stream prior to the catalytic evaluation and following the steps described before [17].

The Pt and/or Co samples supported on Al_2O_3 were subjected to calcination up to 400°C, heating them at 5°C/min and keeping this temperature for 3 h. Table 1 shows details of the preparation of the catalysts.

2.2. Catalytic activity measurement

The reaction was performed in a fixed-bed quartz reactor, 12 mm ID. The catalyst mass was 0.500 g and

Table 1
Composition of catalysts

Samples	Si/Al	Metallic content (%)[a]		Me/Al[b]	
		Co	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	5.9	2.63	0.73	0.19	0.02
$Pt_{0.5}Co_{2.0}$HMor	5.9	1.83	0.30	0.14	0.01
$Co_{2.0}$Mor	5.9	2.91	–	0.29	–
$Pt_{0.5}$Mor	5.9	–	0.37	–	0.01
$Pt_{0.5}Co_{2.0}$ZSM-5	9.7	1.62	0.61	0.18	0.02
$Pt_{0.5}Co_{2.0}$Fer	8.8	1.80	0.56	0.19	0.02
$Pt_{0.5}$Mor + $Co_{2.0}$Mor (Mechanical mixture)	5.9	1.31	0.37	0.1	0.01
$Pt_{0.5}$Mor/$Co_{2.0}$Mor (Two-stage catalyst)	5.9	1.31	0.37	0.1	0.01
Pt/Al_2O_3	–	–	0.5	–	0.002
Co/Al_2O_3	–	2.0	–	0.01	–
$Pt/Co/Al_2O_3$	–	1.64	0.46	0.008	0.002

[a] Percentages of weight in metal were determined by atomic absorption and CPS.
[b] Calculated per unit cell of zeolites in zeolitic catalysts and per gram of catalyst in Al_2O_3 catalyst.

the typical reacting mixture was 1000 ppm of NO, 1000–3000 ppm of CH_4, 2% O_2 balanced at 1 atm in He (GHSV: 6500 and 30,000 h^{-1}). Water was introduced through a saturator in which different concentrations were obtained by varying temperature. The catalytic activity was evaluated with an SRI 9300 B chromatograph with two columns: 5 Å molecular sieve and Chromosorb 102.

The NO conversion (C_{NO}) was calculated by the production of N_2, and the CH_4 conversion (C_{CH_4}) was calculated by consumption: $C_{NO} = 2[N_2]/[NO]^\circ \times 100$; $C_{CH_4} = ([CH_4]^\circ - [CH_4])/[CH_4]^\circ$, where $[NO]^\circ$ and $[CH_4]^\circ$ are the initial concentrations of NO and CH_4, respectively.

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 recorded at various temperatures.

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

The data for NO adsorption was 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.

2.4. XPS experiments

XPS data were obtained in a Shimadzu ESCA-750 spectrometer equipped with an anode for Mg Kα ($h\nu = 1253.6$ eV) radiation. The signal was accumulated and processed using an ESCAPAC 760 computer system. The curve-fitting processing was made using Gaussian–Lorentz profiles in order to be able to detect asymmetries or additional species. 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, and the mean free paths of the electrons. The instrumental function was supplied by the ESCA manufacturer. The binding energy (BE) of Si(2p) was taken as reference, and measured for each support. Results values were: 102.9 (2.5) eV for NaMordenite; 102.8 (2.4) eV for K-Ferrierite and 103.0 (2.2) eV in Na-ZSM-5.

The calcined samples were subjected to the standard pretreatment and dehydration in the high vacuum chamber (slowly heated at the rate of 5°C/min up to 150°C and then up to 350°C) to eliminate the water from the catalyst. Afterwards, the sample was measured at room temperature. It was then reduced for 1 h with H_2 in the pretreatment chamber attached to the analysis chamber, so that the solid was not in contact

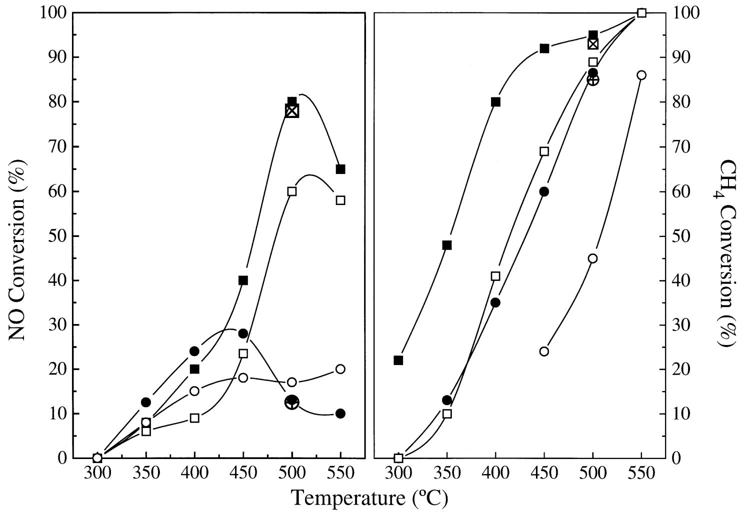

Fig. 1. Conversion rate of NO and CH_4 depending on the reaction temperature for PtCo-Mordenite and Co-Mordenite. ■, □, ☒ $Pt_{0.5}Co_{2.0}$Mor, ●, ◑, ⊗ $Co_{2.0}$Mor. Filled symbols: dry conditions. Empty symbols: wet conditions. Cross-empty symbols: after removal of water from the feed stream. Reaction conditions: GHSV: 6500 h^{-1}, NO: 1000 ppm. CH_4: 1000 ppm, O_2: 2%, Water: 2%, balance to 1 atm with He.

with the atmosphere. After the catalytic evaluation, the catalysts were also analyzed following the dehydration treatment in the analysis chamber described above.

2.5. TPR experiments

Temperature-programmed reduction experiments were performed in an Okhura TP-20025 flow equipment with a TCD detector. 0.1 g of solid was employed and 5% H_2/Ar was used as 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 of a small dead volume with KBr windows was used which allowed treatment in situ. The pellets were self-supported (7–10 mg/cm^2). Before the FTIR experiments, the samples were subjected to the standard pretreatment and dehydrated under vacuum overnight at 400°C. Then, 7 Torr of NO were admitted to the cell at the desired temperature and the spectra were recorded at the same temperature. Their changes with time were also recorded. The spectra from the adsorbed species were obtained by subtracting the spectrum of the water from the spectrum determined after adsorption.

3. Results

3.1. Catalytic results

In a previous study [17] we found that the incorporation of 0.5% of Pt to a 43% base exchange capacity (BEC) Co-Mordenite promoted the SCR of NO_x with methane after the samples had been reduced in H_2 at 350°C for 1 h. With such platinum loading the greatest efficiency of NO to N_2 conversion was obtained. When the Pt content increased, the activity for CH_4 with O_2 combustion was prevalent. Consequently, all the samples investigated in this study were prepared with 0.5% of Pt and pretreated in H_2 before the catalytic tests. The results shown in Figs. 1 and 2 confirm our previous findings both at GHSV = 6500 and 30,000 h^{-1}. When 2% of water vapor was added to the feed stream, both the NO_x to N_2 conversion and the CH_4 to CO_2 conversion of bimetallic as well as monometallic samples decreased (Figs. 1 and 2). Interestingly, in $Co_{2.0}$Mor, while the NO to N_2 conversion dropped to 2% at GHSV = 30,000 h^{-1} and 500°C, $Pt_{0.5}Co_{2.0}$Mor showed 36% of conversion under the

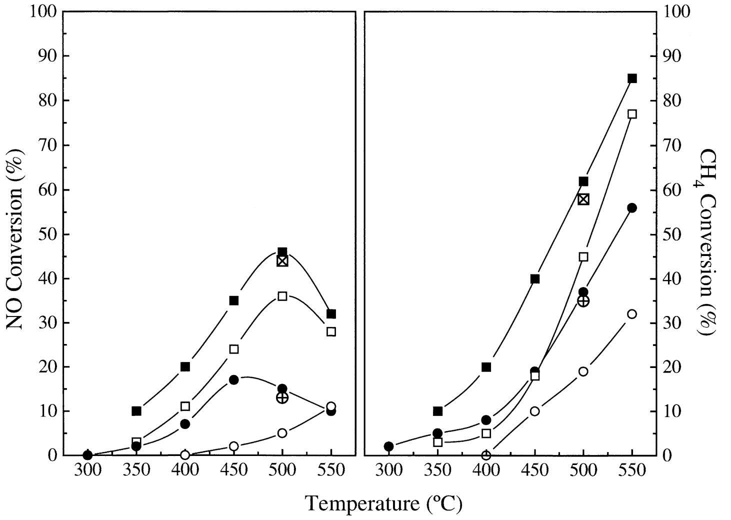

Fig. 2. Conversion rate of NO and CH_4 depending on the reaction temperature for PtCo-Mordenite and Co-Mordenite. ■, □, $Pt_{0.5}Co_{2.0}$Mor, ●, ◑ $Co_{2.0}$Mor. Filled symbols: dry conditions. Empty symbols: wet conditions. Reaction conditions: GHSV: 30,000 h^{-1}, NO: 1000 ppm. CH_4: 1000 ppm, O_2: 2%, Water: 2%, balance to 1 atm with He.

same reaction conditions. Besides, when the water was removed from the feed stream, the activity and selectivity were totally recovered, whereas in $Co_{2.0}$Mor only 80% of the initial NO to N_2 conversion was obtained (Fig. 2). Under comparable reaction conditions ([NO] = 850 ppm, [CH_4] = 1015 ppm, [O_2] = 2.5%, [H_2O] = 2%, GHSV = 30,000 h^{-1}, 500°C) Armor and co-workers [18,19] reported a NO to N_2 conversion of 25, 28 and 29% over Co-Mordenite, Co-ZSM-5 and Co-Ferrierite, respectively. Despite the higher Co/Al ratio (viz. 0.47, 0.49 and 0.39, respectively) of such samples compared to the bimetallic mordenite (Co/Al = 0.21) their NO_x to N_2 conversion was lower. However, the Co-Mordenite used in this study shows a different behavior which could be due to the lower Co loading and/or to the difference in the method of sample preparation (*vide supra*).

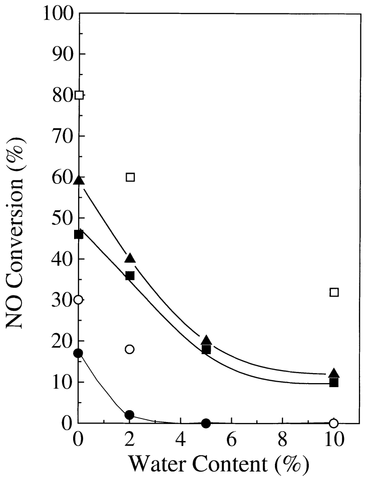

Fig. 3. Conversion rate of NO depending on the water content for $Pt_{0.5}Co_{2.0}$Mor and $Co_{2.0}$Mor. ■, □, $Pt_{0.5}Co_{2.0}$Mor (CH_4/NO: 1), ▲ $Pt_{0.5}Co_{2.0}$Mor (CH_4/NO: 3), ●, ◑ $Co_{2.0}$Mor (CH_4/NO: 1). Filled symbols: GHSV: 30,000 h^{-1}, empty symbols: GHSV: 6500 h^{-1}. Reaction conditions: NO: 1000 ppm. CH_4: 1000–3000 ppm, O_2: 2%, balance to 1 atm with He, Temperature: 500°C.

To further investigate the promotion effect of Pt on the activity of Co-Mordenite under a wet reaction stream, the role of water vapor concentration on the SCR of NO_x was studied at GHSV = 30,000 h^{-1}. The results obtained at two CH_4/NO ratios (viz. 1 and 3) are shown in Fig. 3. The NO_x conversion of the bimetallic mordenite strongly decreased up to 5% of water in the feed stream but with further increases of the H_2O level, its impact on NO conversion was rather mild. The effect of H_2O over $Pt_{0.5}Co_{2.0}$Mor was no function of the level of CH_4 in the feed (Fig. 3). Besides, the bimetallic Co-Pt-Mordenite remains stable (NO to N_2 about 40%) for more than 250 h under reaction stream (NO = CH_4 = 1000 ppm, 2% O_2, 2% water vapor, GHSV = 30,000 h^{-1}). This is differ-

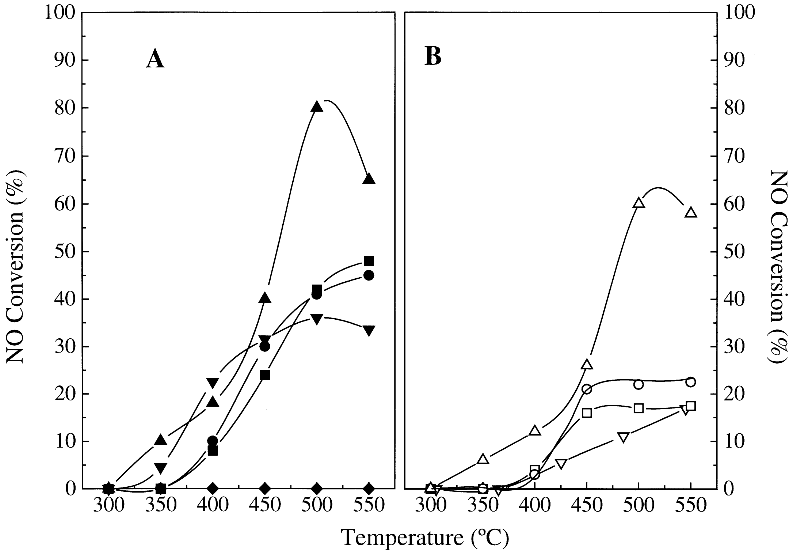

Fig. 4. Conversion rate of NO depending on the reaction temperature for various catalysts set up. ▲, △ $Pt_{0.5}Co_{2.0}Mor$, ▼, ▽ $Co_{2.0}Mor$, ◆, $Pt_{0.5}Mor$, ●, ◑ $Pt_{0.5}Mor + Co_{2.0}Mor$ (mechanical mixture), ■, □ $Pt_{0.5}Mor/Co_{2.0}Mor$ (two-stage catalyst). (A) Dry conditions, (B) wet conditions. Reaction conditions as in Fig. 1.

ent from the behavior of Co-ZSM-5 reported by Li et al. [18,25]. Besides, while this catalyst presented a NO conversion of about 15% at 500°C with 7.3% of water in the feed stream at GHSV of $7500\,h^{-1}$ and a CH_4/NO ratio of 4 [20], the bimetallic mordenite converted 32% of NO with $CH_4/NO = 1$ and a comparable GHSV (Fig. 3). In the same vein, Ogura et al. [12], in their study of the effect of the coexistence of Pd and Co on H-ZSM-5, reported a NO to N_2 conversion of 12% at 400°C with $CH_4/NO = 2$, 10% O_2, and 10% H_2O in the feed stream at $GHSV = 11{,}400\,h^{-1}$ over the bimetallic samples. On the contrary, Co-HZSM-5 was not active under these reaction conditions. The positive role of Pt on the water resistance of Co-Mordenite appeared again when the bimetallic sample was compared with the monometallic one. In fact, for the latter the NO conversion dropped to zero when less than 5% of water was added to the feed stream.

In order to determine whether the promotion effect of Pt on Co-Mordenite activity needs the intimate contact of cations, or if it is only a consequence of the presence of platinum, the following two sets of experiments were conducted:

(i) A mechanical mixture of both calcined monometallic solids was prepared so as to obtain a sample with comparable Co/Pt ratio as the bimetallic ones. The mixture was reduced at 350°C for 1 h in H_2 flow and then it was catalytically evaluated under the same conditions as the bimetallic sample;

(ii) A two-stage catalyst was prepared. It consisted of $Pt_{0.5}Mor$ (upstream) and $Co_{2.0}Mor$ (downstream) in two layers separated by a layer of quartz wool with an overall Co/Pt ratio similar to the bimetallic sample. In this case, the catalyst was also reduced as before and then catalytically tested. In Fig. 4A, the NO to N_2 conversion of the above combination (mechanical mixture and two-stage catalyst) is compared with the reduced monometallic ($Co_{2.0}Mor$, $Pt_{0.5}Mor$) and bimetallic ($Pt_{0.5}Co_{2.0}Mor$) samples. Up to 500°C, the N_2 yield of both the mechanical mixture and the two-stage catalysts were comparable. The overall N_2 yield of both catalytic systems was higher than the sum of the individual yields of $Co_{2.0}Mor$ and $Pt_{0.5}Mor$, but such yield was lower than in the bimetallic catalysts. When 2% of water was added to the feed stream, an increase in the difference with the bimetallic catalyst was observed (Fig. 4B). This suggests that an intimate contact of the active sites in the zeolite channel was necessary to improve the promotion effect of Pt.

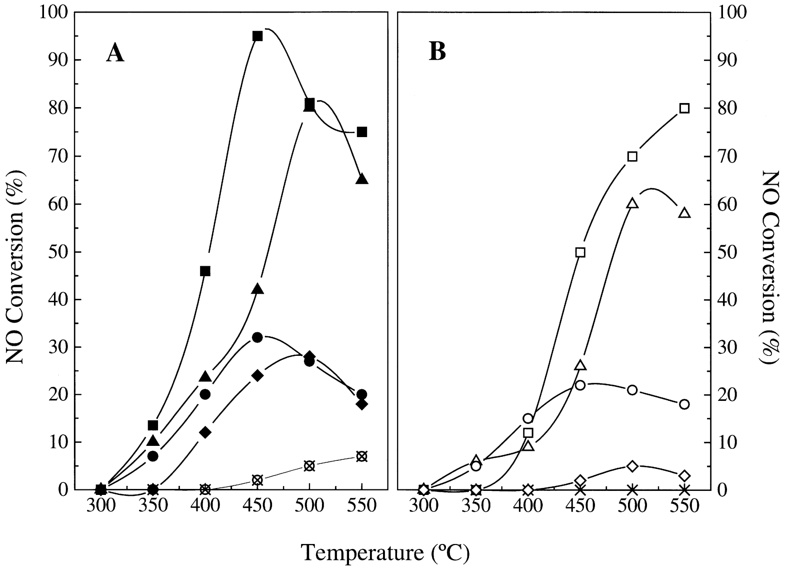

Fig. 5. Effect of support on conversion rate of NO under wet reaction stream. ▲, △ $Pt_{0.5}Co_{2.0}$Mor, ■, □ $Pt_{0.5}Co_{2.0}$Fer, ●, ◑ $Pt_{0.5}Co_{2.0}$ZSM-5, ◆, ◇ Pt/Co/Al_2O_3, ⊗, X Co/Al_2O_3. (A) Dry conditions, (B) wet conditions. Reaction conditions as in Fig. 1.

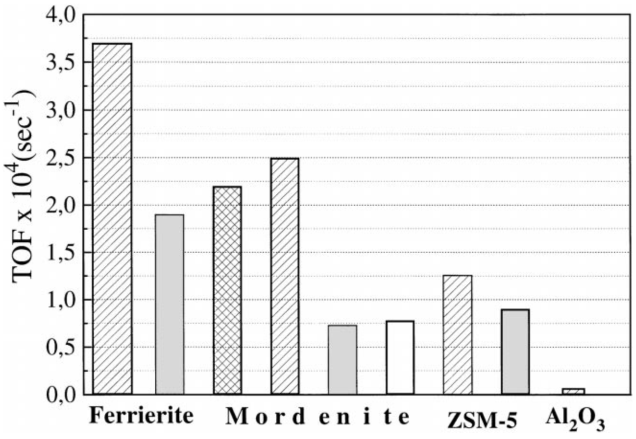

Fig. 6. NO_x turnover frequencies for various catalysts. ▨ $Pt_{0.5}Co_{2.0}$Fer, ■ $Co_{2.0}$Fer, ▩ $Pt_{0.5}Co_{2.0}$HMor, ▨ $Pt_{0.5}Co_{2.0}$Mor, ■ $Co_{2.0}$Mor, ▨ $Pt_{0.5}Co_{2.0}$ZSM-5, □ $Pt_{0.5}$Mor + $Co_{2.0}$Mor, ■ $Co_{2.0}$ZSM-5, ▨ Pt/Co/Al_2O_3. Reaction conditions: NO: 1000 ppm, CH_4: 1000 ppm, O_2: 2%, H_2O: 2%, balance to 1 atm with He, GHSV: 6500–100,000 h^{-1} to keep C_{NO} below 20%. Monometallic samples were calcined by standard pretreatment. Bimetallic samples were reduced after standard calcination.

To further investigate this effect, bimetallic samples were prepared on different zeolites (viz. ZSM-5, ferrierite and Y-zeolite) and on Al_2O_3 support, and catalytically evaluated after reduction at 350°C for 1 h in H_2 flow. The incorporation of Pt increased the NO to N_2 conversion (Fig. 5A) and the intrinsic activity of cobalt exchanged in the different zeolite structures (Fig. 6). The Co-zeolites showed the same trend previously reported by Armor [20] but they proved less active when the Co loading was taken into account (Fig. 6). However, the bimetallic samples presented a better activity for the SCR of NO (Fig. 6) [19]. An interesting behavior was observed on Y-zeolites and Al_2O_3. Whereas the former proved inactive for both mono and bimetallic solids, Co/Al_2O_3 and Pt/Al_2O_3 were almost inactive in the latter within the temperature range under study, but Pt/Co/Al$_2$O$_3$ reached 30% NO to N$_2$ conversion at 500°C.

Fig. 5B shows the results obtained when 2% water was added to the feed-stream. The overall N$_2$ yield was lower in all the catalysts but while in the bimetallic ferrierite, mordenite and ZSM-5, NO to N$_2$ conversions of 70, 60 and 20%, respectively, were reached at 500°C, in Pt/Co/Al$_2$O$_3$ that conversion was less than 5%.

In search for a better understanding of the Pt promotion effect and in an attempt to elucidate the nature of the active sites, gravimetric and FTIR studies of NO adsorption were performed and the solids were also studied by TPR techniques and XPS. In this paper, those studies were focused on the mono and bimetallic mordenite samples.

3.2. NO adsorption results

With the purpose of studying the effect of Pt on the capability of the catalyst to adsorb NO, the adsorption of such species was measured on mono and bimetallic mordenites using a microbalance for quantitative results and FTIR techniques to characterize the species formed. The studies were conducted at different temperatures. Some of the preliminary data obtained at 300°C are shown in Figs. 7 and 8.

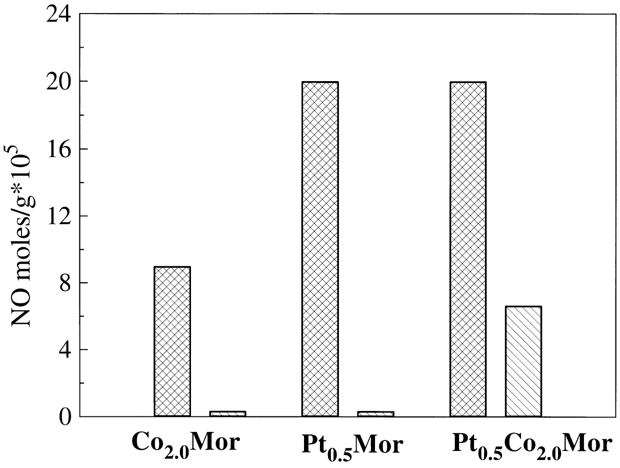

Fig. 7. Microbalance data for the NO adsorption. ▩ Reversible adsorption, ▧ irreversible adsorption (after 1 h flowing He at 300°C). Temperature: 300°C, adssorption time: 60 min. The catalysts were pretreated in flowing O$_2$ overnight, purged with dry He for 1 h, cooled in He flow before contacting with a stream of 5% of NO in He.

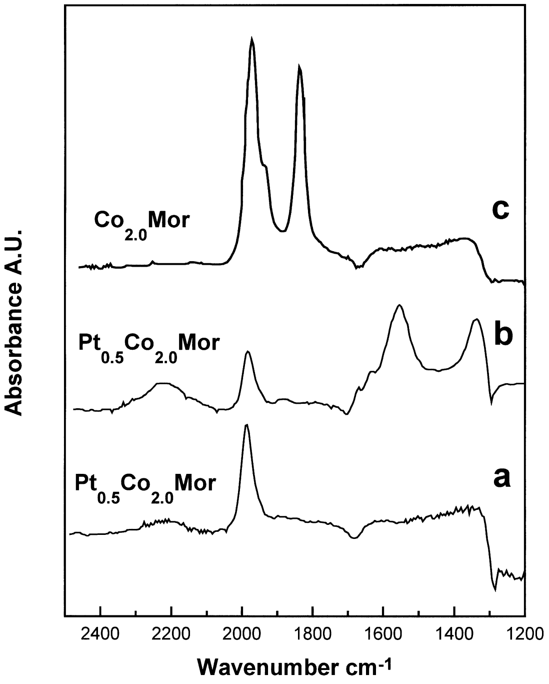

Fig. 8. FTIR spectra obtained from NO adsorption on Pt$_{0.5}$Co$_{2.0}$Mor after (a) 1 min contact time, (b) 10 min contact time and Co$_{2.0}$Mor after: (c) 1 and 10 min contact time. See Section 2.

The results obtained on Co$_{2.0}$Mor are in general agreement with our previous findings [17] and those of Zhang et al. [21]. In fact, they reported a NO/Co ratio of 0.25 molecules NO$_x$/Co^{2+} at 250°C on Co-Mordenite (Si/Al = 5.25, 65% BEC) against 0.19 molecules/Co^{2+} at 300°C (Si/Al = 5.9, 43% BEC) in this work (Fig. 7). Calcined and reduced Pt$_{0.5}$Co$_{2.0}$Mor adsorbed the same amount of NO (viz. NO/Co^{2+} = 0.42), which was higher than in the monometallic samples. Interestingly, after 1 h under flowing He at 300°C, the NO adsorbed on both the mono and calcined bimetallic mordenites was totally removed, whereas in the reduced Pt$_{0.5}$Co$_{2.0}$Mor, 0.12 NO/Co^{2+} remained adsorbed. No reoxidation by NO of the reduced sample was observed under such conditions.

The IR spectrum obtained from Co$_{2.0}$Mor and Pt$_{0.5}$Co$_{2.0}$Mor in the presence of 7 Torr of NO at 300°C at various time intervals is shown in Fig. 8. After 1 min, bands at 1878, 1900 and 1934 cm^{-1} appeared in the monometallic samples and remained constant with time. In agreement with Ailer et al.

Table 2
XPS data of PtCo-Mordenites

Catalyst	Treatment	$Co(2p_{3/2})$ Binding energy (eV)[a]				$(Co/Si)_s$[b]
		Co^{+2}	Co^0	Pt^{+2}	Pt^0	
Co/SiO_2	Calcined 400°C	781.5	–	–	–	0.22
	Reduced 350°C	–	778.2	–	–	0.08
$Co_{2.0}Mor$	Calcined 400°C	783.1	–	–	–	0.09
	Reduced 350°C	783.4	–	–	–	0.05
$Pt_{0.5}Co_{2.0}Mor$	Calcined 400°C	783.1	–	–	–	0.08
	Reduced 350°C	783.3	–	–	–	0.05
	After reaction (dry)[c]	783.2	–	–	–	0.14
	After reaction (wet)[c]	783.3	–	–	–	0.12
$Pt_{1.0}Co_{2.0}Mor$	Calcined 400°C	783.1	–	73.1	71.9	0.08
	Reduced 350°C	783.3	778.3	73.1	71.9	0.08
$Pt/Co/Al_2O_3$	Calcined 400°C	782.5	–	–	–	0.08[d]
	Reduced 350°C	782.0	–	–	–	0.17[d]

[a] The binding energy values are referred to Si(2p): 102.9 (2.5) eV for NaMordenite and 103.8 eV for SiO_2.

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

[c] Reaction conditions: GHSV: 6500 h^{-1}, NO: 1000 ppm, CH_4: 1000 ppm, O_2: 2%, H_2O: 2% balanced to 1 atm with He.

[d] Co/Al ratio.

[22], those bands could be assigned to dinitrosyl and mononitrosyl species, respectively. In the bimetallic sample, only a band centered at 1934 cm^{-1} can be observed after 1 min of contact with NO. As the contact time increased, such a band decreased and new bands appeared at 1312 and 1510 cm^{-1} which were assigned to adsorbed NO_2 species. This suggested that disproportion of NO ($3NO \leftrightarrow N_2O + NO_2$) takes place in bimetallic samples, as suggested by Lunsford et al. [23] for other zeolites.

3.3. XPS results

Bimetallic PtCo-Mordenite, monometallic Co-Mordenite and also Co/SiO_2 and $Pt/Co/Al_2O_3$ were analyzed by XPS. The measurements were performed in the BEs region corresponding to Si(2p), Al(2p), Pt(4f), Co(2p) and C(15). Al(2p) was also measured in the NaMordenite obtaining a BE value of 74.5 eV with a full width at half maximum = 2. The samples were analyzed after various treatments: (a) Calcination, (b) in situ reduction at 350°C, (c) after reaction under dry stream for several hours, (d) after reaction with 10% of vapor water added to the feed stream for several hours. Some of the results obtained are summarized in Table 2.

The Pt(4f) signal partially overlapped 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 higher platinum loading were studied, the binding energies of Pt^{2+} and Pt° were detected in both calcined and reduced samples (Table 2).

In the bimetallic solids subjected to the different treatments mentioned before, the Al(2p) BE was modified only at ±0.2 eV. In the sample with 0.5 wt.% of platinum, the only signal observed was the one at 783.2 ± 0.1 eV, which can be assigned to the ion of Co^{2+} located at exchange position, in agreement with what was reported by several authors [24,25]. This is also confirmed if we compare the $Co(2p_{3/4})$ BE of the cobalt on mordenite with that one supported on SiO_2 (Table 2). Only in the sample with higher Pt loading (viz. $Pt_{1.0}Co_{2.0}Mor$) after reduction with H_2 at 350°C did the Co^{2+} (783.3 eV) and Co° (778.3 eV) signals coexist. The BE metallic cobalt was comparable to the solids used after reaction. The Co/Si surface ratio was higher than the bulk one (compare Tables 1 and 2). Such surface ratio increased in the solid after being under a reaction stream. Interestingly, it was not affected by the presence of up to 10% of water in the feed stream (Table 2).

3.4. TPR results

With the aim of obtaining additional information about the Pt–Co interaction, TPR experiments were performed on monometallic Co and PtMordenites

Table 3
Reducibility of Co and PtMordenite

Catalyst	µmoles of metal[a]		µmoles of H_2[b]		H_2/(Co+Pt)[c,d]
	Co	Pt	20/400°C	400/800°C	20/800°C
$Co_{2.0}$Mor	20.2	–	–	8.90	0.44
$Pt_{0.5}$Mor	–	1.90	1.34	0.57	1.00
$Pt_{0.5}$Mor + $Co_{2.0}$Mor (mechanical mixture)	27.6	1.90	3.35	9.90	0.42
$Pt_{0.5}$Mor/$Co_{2.0}$Mor (two-stage catalyst)	27.6	1.90	2.40	9.10	0.39
$Pt_{0.5}Co_{2.0}$Mor	24.0	1.65	4.70	20.95	1.00
$Pt_{0.5}Co_{2.0}$Mor (after reaction dry conditions)	24.0	1.65	–	21.60	0.84
$Pt_{0.5}Co_{2.0}$Mor (after reaction wet conditions)	24.0	1.65	2.40	21.0	0.91

[a] µmoles of metal used in TPR experiment.
[b] H_2 consumption from TPR profile.
[c] H_2 consumption per (Co + Pt) moles.
[d] H_2 consumption per Co moles (the one corresponding to Pt was subtracted from the total H_2 consumption).

on the two combinations described before (viz. mechanical mixture and two-stage catalyst), and on the bimetallic PtCo-Mordenite. The results obtained are shown in Fig. 9 and Table 3.

In agreement with our previous findings [17] the H_2 consumption in $Pt_{0.5}$Mor indicated that one molecule of H_2 is consumed per platinum (Table 3). This would indicate that the average oxidation state of platinum remains divalent after calcination at 350°C. The TPR profile of $Co_{2.0}$Mor presented a broad peak with a maximum at 550°C. The H_2 consumption per Co mol indicates that an overall reduction of 44% was reached under the TPR experimental conditions.

The TPR profile of the mechanical mixture and the two-stage catalyst appear to be qualitatively very similar and equal to the sum of the individual TPR profiles of the monometallic mordenite (Fig. 9). However, from a quantitative point of view some difference became visible in the lower temperature zone. In fact, the H_2 consumption in this zone indicated that in the mechanical mixture 5% of cobalt was reduced, whereas in the two-stage catalyst the degree of reduction of the Co was 2%. In the mechanical mixture some interaction of Pt and Co could be expected which could affect the reducibility of the cobalt in the zeolitic matrix. Such interaction could also be due to the mobility of Co-Mordenite during the O_2 treatment at 400°C (*vide supra*). This effect was less probable in the two-stage catalyst. The greater than expected increase in the H_2 consumption observed in such samples cannot be explained with the data obtained so far.

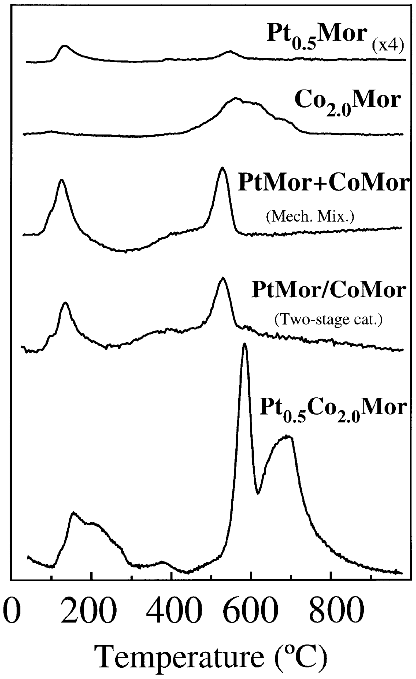

Fig. 9. Reducibility of various catalysts.

The reduction profile of the bimetallic $Pt_{0.5}Co_{2.0}$Mor catalyst did not correspond to the sum of its respective monometallic samples (Fig. 9). In the below 400°C temperature zone, the H_2 consumption indicated that 13% of the cobalt was reduced, whereas at higher temperatures the remaining 87% was reduced. Noticeably, in this higher temperature region, two well-defined peaks were observed, while in the $Co_{2.0}$Mor there was only one broad peak which started at approximately 420°C and finished at about 750°C. The increase in the reducibility of Co (Table 3) and

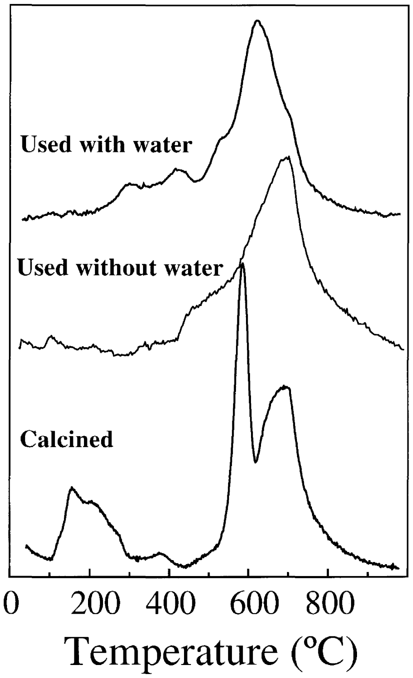

Fig. 10. Influence of water on the reducibility of $Pt_{0.5}Co_{2.0}$Mor.

the different shapes of TPR profiles (Fig. 10) strongly suggest a promotion effect of Pt on the reducibility of Co exchanged in mordenite when both coexist in the same zeolite structure. Compare $Pt_{0.5}Co_{2.0}$Mor TPR profile with that of the PtMordenite/Co-Mordenite mechanical mixture (Fig. 9).

The reducibility of the bimetallic mordenite after being under reaction stream with and without water in the feed was also studied by temperature-programmed reduction. In Fig. 10, the TPR profiles of both used catalysts are compared with the fresh calcined $Pt_{0.5}Co_{2.0}$Mor. Both used samples under dry and wet reaction stream (10% of water in the feed-stream) present comparable TPR profiles and they are different from that of the calcined samples.

The used samples did not present the expected TPR peak with a maximum at temperatures lower than 250°C. The catalyst that was not exposed to a wet stream started to reduce at 400°C producing a peak with a maximum approximately at 700°C. The sample that had been several hours (more than 100) in feed reaction stream with 10% of water vapor presented a small peak in the lower temperature zone with a maximum about 300°C. This could suggest that part of the cobalt was segregated as a consequence of the wet reaction stream and would form supported cobalt oxides. If this was the case, the H_2 consumption per Co molecule indicated that 10% of the total cobalt was segregated (Table 3).

4. Discussion

In agreement with what ever has been reported elsewhere [17] the addition of 0.5% Pt to Co-exchanged zeolites promoted the NO to N_2 conversion when CH_4 was used as a reducing agent increasing the intrinsic activity of Co in the zeolite matrix (Figs. 1, 2, 5 and 6). The addition of up to 10% water to the feed stream did not seem to totally affect the conversion values. These, however, dropped to zero in the $Co_{2.0}$Mor when 5% of water was added to the feed stream (1000 ppm NO, 1000 ppm CH_4, 2% O_2) at 500°C and a GHSV = 30,000 h^{-1}. The $Pt_{0.5}Co_{2.0}$Mor showed 20% of NO_x conversion. This N_2 yield, though not very high, appeared promising when compared with the ones repeated over different monometallic as well as bimetallic Co-zeolites [12,20] (*vide supra*).

The promotion effect became evident when the solids were reduced in H_2 flow for 1 h at 350°C. After such pretreatment, XPS only detected Co^{2+} located at exchange position. No significant changes in the BE of $Co(2p_{3/2})$ were detected after the catalysts had been under reaction for several hours either with or without water in the feed-stream. Despite the fact that TPR results revealed that 13% of Co (0.4% of the total Co loading) was reduced after treatment in H_2 at 350°C (Fig. 9, Table 3), the signal corresponding to the BE of supported Co° was detected neither in reduced samples (fresh catalyst) nor in samples placed under a dry or wet reaction stream. This could be due to the low amount of such species. In fact, when samples with 1% of Pt were analyzed after reduction, the Co° signal was detected in the XPS spectra. The BE of Co° in $Pt_{0.5}Co_{2.0}$Mor is comparable to that of Co°/celite (Table 2), suggesting that no formation of Pt–Co bimetallic particles takes place [24].

From the TPR experiments it can be inferred that Pt° particles were formed after the reduction treatment (Fig. 9, Table 3). This species seemed to be stable after the catalyst had been under dry as well as wet reaction streams (Fig. 10, Table 3). However, XPS did not detect Pt° signals in samples with 0.5 wt.% loading. This species became visible in samples with 1 wt.% Pt loading. Pt° and Pt^{2+} were present in all the samples studied (viz. calcined and reduced).

This complex system yields very active and selective catalysts for the SCR of NO with CH_4 but in order to elucidate such behavior, some queries need to be answered.

- Is a close interaction among the different species necessary to obtain the desired effect?
- Do all the species present play a role in the enhancement of the activity of such catalysts?
- Which are the factors responsible for the promotion effect of Pt on Co-zeolites?

The NO to N_2 conversion of the mechanical mixture of $Co_{2.0}$Mor and $Pt_{0.5}$Mor and the two-stage catalysts at temperatures higher than 450°C (Fig. 4) would indicate that the catalytic behavior of such samples under dry reaction conditions is not a consequence of the sum of the individual effects. Some promotion effect of Pt appears to have occurred, but it was almost canceled when water was added to the feed stream (Figs. 1A, 4A and 4B). In the bimetallic systems such promotion effect of platinum was most evident and it remained even with high levels of water in the feed stream (Figs. 1A, 2A and 3). This shows that in order to obtain a more efficient catalyst of the SCR of NO_x with CH_4, Pt and Co need to be in intimate contact inside the channel or on the surface of the mordenite. The above behavior exhibits similarities and discrepancies with comparable catalytic systems which present the cooperative effect between active species. In fact, Yan et al. [13] reported a synergetic effect in lean NO_x reduction by CH_4 over physical mixtures of Co/Al_2O_3 and H-zeolite at temperatures above 500°C ($CH_4/NO = 3$, $O_2 = 2\%$, GHSV = 14,000 h^{-1}) but they did not find such effect when H-ZSM-5 (upstream) and Co/Al_2O_3 (downstream) were used as two layers separated by a layer of quartz wool. The authors did not report catalytic tests with water in the feed stream. They concluded that the synergetic effect could be explained by the participation of Co ions and protons. NO is oxidized to NO_2 over the Co ions and NO_2 is reduced by CH_4 to N_2 over the proton sites. Loughran and Resasco [5] also reported a bifunctional catalyst when they studied the combination of Pd and H-ZSM-5. They found that if H-ZSM-5 was mechanically mixed with Pd/SiO_2, the resulting activity for the SCR of NO_x with CH_4 was much lower than that of the palladium directly supported on H-ZSM-5. By contrast, if SO_4^{2-}/ZrO_2 was mechanically mixed with Pd/SiO_2, the resulting activity showed about the same conversion level as observed when Pd is directly supported on SO_4^{2-}/ZrO_2. They concluded that both palladium and acid sites are necessary to achieve high catalytic activity and that the two catalytic functions do not need to be in intimate contact to generate an effective SCR catalyst. However, the authors assumed that the different behavior observed with H-ZSM-5 was due to the limitation transfer of reaction intermediates from palladium to the acid sites or vice versa through zeolite cages. This conclusion appears to be in disagreement with the one reached by Yan et al. [13] (*vide supra*). The results obtained with the Pt/Co/zeolite system suggest that up to a certain extent there is some cooperation between species, even when they may not be in intimate contact. A close interaction among them enhances such cooperation effect and consequently yields a better catalyst for the SCR of NO_x with CH_4. The presence of water vapor seems to interfere with the transportation of reaction intermediates from one site to the other, both in the mechanical mixture and in the two-stage catalyst. This interference is not so pronounced when the active sites are located in the same zeolite structure (viz. PtCo-Mordenite) (Fig. 4). The different behavior of the bimetallic samples could also be due to the fact that such solids are uniform catalysts containing two or more catalytic species whose role is sometimes difficult to determine [8].

At this point, the role of the support has to be emphasized. It affects both the intrinsic activity of the active species and their performance under wet reaction stream (Figs. 5 and 6). The difference in activity and selectivity between Co exchanged on various zeolite structures has been reported by Li and Armor [19]. The authors found the following order in activity and selectivity: Co-Ferrierite > Co-ZSM-5 > Co-Mordenite. They explained those results by assuming that the different location and coordination of Co^{2+} in the zeolite channels would affect their activity and selectivity. The restriction of the diffusion of methane molecules by small channels may control the selectivity to methane. The monometallic Co-zeolites in this study kept the same order (Fig. 6), whereas in the bimetallic samples the order was: PtCo-Ferrierite > PtCo-Mordenite > PtCo-ZSM-5≫

$Pt/Co/Al_2O_3$. This suggests that when Pt is incorporated to Co-zeolites, some changes in the nature and/or accessibility of the active sites seem to occur (*vide infra*).

The water resistance of the PtCo-zeolites appears to be independent of the zeolite channels topology but strongly dependent on the support structure (viz. zeolite against Al_2O_3) (Fig. 5). This could be related to the relative accessibility of the active site to water molecules.

As discussed before, the species that the reaction stream 'could see' are: Pt°, Co°, Pt^{2+}, Co^{2+} (Table 3, Figs. 9 and 10) and, eventually, some Brönsted acid sites formed during the H_2 reduction of the samples [16,26]. In order to understand the role of such species and how they contribute to enhance the activity of the bimetallic samples, several well-documented facts about the SCR of NO should be introduced.

NO_2 has been proposed by various authors as an important intermediate in the reaction scheme [20,27,28]. The bifunctional mechanism has been formulated by a combination of acidity and metal species like Ga/H-ZSM-5 and In/H-ZSM-5 [29]. In this case, the authors suggested that the $NO + (1/2)O_2 \rightarrow NO_2$ reaction occurred in the zeolitic acid sites. In this study, we found that the TOF of PtCo-Mordenite (the H^+ in this sample came only from H_2 reduction) and PtCoHMordenite were comparable (Fig. 6) despite the bigger amounts of Brönsted sites in the latter. This suggests that the H^+ generated during reduction does not play an important role.

The reduced Co/Al_2O_3 where cobalt has been reduced 100% to Co° was almost inactive for the SCR of NO_x. Yan et al. [13] also reported a very low activity of calcined Co/Al_2O_3 (viz. less than 10% of NO to N_2 conversion at 500°C) [$CH_4/NO = 3$, $O_2 = 2\%$, $GHSV = 14{,}000\,h^{-1}$). Hence, neither Co° nor Co^{2+} or Co_2O_3 contributed to the enhancement of bimetallic solids activity. Further evidence could be derived from the analysis of the TPR results of the catalyst used under wet reaction stream (Fig. 10) and the catalytic behavior when water was removed from the feed stream (Figs. 1 and 2). In fact, when water was removed from the feed stream, both the activity and selectivity of PtCo-Mordenite were totally recovered. On the contrary, the TPR profile shows that part of the cobalt which was reduced at low temperature segregated and then formed supported cobalt oxides. This did not occur when the catalytic test was performed without water in the feed stream. Consequently, it seems that those species did not participate as active sites in the reaction scheme.

A similar bifunctional mechanism in the SCR of NO with CH_4 under dry and wet reaction stream was suggested by Kikuchi and co-workers [9–11,30] over In/H-ZSM-5 zeolite promoted with additives such as Pt, Rh, In, Pd, Fe, Ce, etc. In these catalysts the oxidation of NO to NO_2 takes place on the additive metal, whereas the reduction of NO_2 by CH_4 occurs on In sites. The authors also suggested that the role of the precious metal not only enhances the catalytic activity for NO oxidation but also increases the amount of chemisorbed NO_2 species on InO^+ sites [29]. This could also be a suitable explanation for the promotion effect of platinum on Co-zeolites. In the mechanical mixture and in the two-stage catalysts, the high activity of Pt for NO oxidation [14,15] would play the central role in the enhancement of the activity of such catalytic system [31]. In the bimetallic PtCo-zeolites, 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_x as suggested by the results obtained in the NO adsorption on the reduced samples (Fig. 7). This could also increase the amount of NO_2 adsorbed on Co^{2+} located at exchange sites (Fig. 8). A synergetic effect can also occur among the different sites (viz. Pt°, Pt^{2+}, Co^{2+}, H^+) in intimate contact in an adequate zeolite structure. In this scheme Pt^{2+} in zeolite sites may help activate CH_4 to react with the NO_2 adsorbed on Co^{2+} [32] and form CH_3 radicals [33,34]. The protonic acid sites may also favor the NO_2 formation. In the same vein, Loughran and Resasco [5] for the SCR of NO_x with CH_4 over Pd/H-ZSM-5 and Ogura et al.[12] for the said reaction on PdCo-Mordenite, suggested that Pd^{2+} and acid sites and highly dispersed Pd^{2+} and Co^{2+} species, respectively, were necessary to yield a suitable catalyst for the SCR of NO_x, probably due to a synergetic effect among such species.

5. Conclusions

- A promotion effect was observed for the NO reduction to N_2 by CH_4 when Pt and Co exchanged in zeolites were combined. Such effect was a function of the degree of interac-

tion of the active species (Figs. 1, 2 and 4A). $Pt_{0.5}Co_{2.0}Mor > PtMordenite + Co\text{-}Mordenite$ (mechanical mixture) $\cong$ PtMordenite/Co-Mordenite (two-stage catalyst) $> Co_{2.0}Mor$. $Pt_{0.5}Mor$ was inactive under the reaction conditions used.
- Pt strongly enhanced the water resistance of Co-zeolites when both cations were located in the same structure. This effect was not present in either the mechanical mixture or in the two-stage catalysts (Figs. 1, 2 and 4B). The zeolite structure also played a central role in such effect. $Pt/Co/Al_2O_3$ was almost inactive under wet reaction stream (Fig. 5).
- The intrinsic activity of Pt promoting catalysts depends on the support and the zeolite matrix. The order of activity (under wet reaction stream) expressed as turnover frequency (Fig. 6) was $Pt_{0.5}Co_{2.0}Ferr > Pt_{0.5}Co_{2.0}Mor \cong Pt_{0.5}Co_{2.0}HMor > Pt_{0.5}Co_{2.0}ZSM\text{-}5 > Pt_{0.5}Mor /Co_{2.0}Mor$ (mechanical mixture) $\gg Pt/CoAl_2O_3$.
- XPS and TPR results show that the species the reactant sees are Pt°, Pt^{2+}, Co^{2+}, Co° and some H^+ generated during reduction [17]. Such species remain under dry and wet reaction conditions but some reorganization occurs (Tables 2 and 3, Figs. 9 and 10). The catalysts obtained proved to be stable under dry and wet conditions in the temperature range studied.
- The highest activity and selectivity of the PtCo-zeolite could be explained as a synergetic effect (cooperative effect) of the active species (Pt° and exchanged Pt^{2+}, Co^{2+} and H^+) which increased the activity for the NO to N_2 reaction and the activation of CH_4. It also enhances the ability of the catalyst to adsorb NO (Figs. 1, 2, 6, 7 and 8).
- The results obtained with the bimetallic PtCo-zeolites as multifunctional catalysts are very promising. However, more studies on such systems are necessary to conclude that they are suitable catalysts under real reaction conditions.

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