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Binder effect upon the catalytic behavior of PtCoZSM5 washcoated on cordierite monoliths

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Abstracts

PtCoZSM5 in powder form is an effective catalyst for the selective reduction of NO_x with methane. In order to attach a stable film of this powder to a cordierite honeycomb monolith, several approaches were assayed. Either NaZSM5 or CoNaZSM5 were washcoated on the cordierite, and then either Co and Pt or Pt, respectively, was ion exchanged to obtain the desired composition. Another option explored was to washcoat the PtCoZSM5 powder. $Al(NO_3)_3$ used as a binder produced undesirable changes in the catalytic behavior due to the formation of non-stoichiometric cobalt aluminate during the calcination of the monolith at 550 °C. The powder performance was matched when PtCoZSM5 was washcoated without binder. Inspection of the monolith after 80 h on stream showed no deterioration.
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Keywords: PtCoZSM5; Zeolite washcoated monoliths; NO_x + CH_4; Cobalt species; TPR-Raman

1. Introduction

The selective catalytic reduction of NO_x with hydrocarbons and particularly with methane is one of the most studied pathways to abate emissions of these oxides in flue gas from stationary sources [1,2]. In order to obtain more active and water resistant catalysts, the cooperation effect of catalytic species has recently been studied. Kikuchi and co-workers [3,4] performed several studies on the effect of the addition of precious metals (Pt, Rh and Ir) to InH-ZSM5. They reported that such solids are highly selective for the reduction of NO with CH_4 in feed streams containing up to 10% water vapor. The role of the precious metals would be to accelerate the NO oxidation and to increase the NO_2 adsorption capacity even in the presence of water. These authors also suggested that the bifunctional catalysis of such solids is remarkably facilitated by the co-existence of the active sites in the pore of the zeolite, what they call "intrapore catalysis".

In our group, we have characterized the active species and their role in the reaction mechanism for PtIn and PtCo exchanged in ZSM5, ferrierite and mordenite structures [5–8]. Particularly, we found that PtCo zeolites are very active and selective catalysts for N_2 production. They are more selective than Co zeolites and show an enhanced water resistance [5,6]. We suggested a synergistic effect between the metals, the more active catalysts consisting in exchanged Co^{2+} (responsible for NO_x reduction with methane) and Pt–Co_xO_y moieties, mainly responsible for NO oxidation. In some cases, and depending on exchange and calcination conditions, Co_3O_4 crystals can be formed which constitute a non desired species since they only promote the methane oxidation with oxygen, leading to non-selective catalysts [9].

In order to use the PtCo system in combustion exhausts, the powder material has to be washcoated on cordierite

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monoliths. The attachment of the zeolite powder is not a trivial matter. On the other hand, abundant information is available even in the open literature concerning the washcoating of alumina, the material used in commercial three-way catalysts [10].

Under practical conditions, washcoated monolithic catalysts are subjected to high gaseous flow rates and temperature fluctuations. As a result, adhesion loss is a likely cause for concern. Although adhesion is a more critical factor for vehicle catalysts, for stationary sources the loss of the catalytic washcoat via attrition or erosion is also a serious source of irreversible deactivation. To improve the coating adherence, a binder is usually employed, consisting in different oxides (alumina, silica) or precursors of them as metal nitrates. Among them, alumina is probably the most frequently used in three-way catalysts. The function of these oxides is to provide a bind between the catalyst particles and the monolith, without affecting the catalyst performance. $Al(NO_3)_3$ was used as binder to washcoat CuZSM5 to cordierite. The monoliths were used in the SCR of NO with hydrocarbon [11–13]. Our group has recently prepared a PtCoFer-washcoated cordierite monolith by adding SiO_2 as binder. This formulation resulted in active and thermally stable in the SCR of NO with CH_4 in the presence of water [14].

In this work, we have studied the procedure to obtain an active, stable catalyst made up of PtCoZSM5 washcoated on cordierite. Among other things, particular attention has been paid to the addition of a binder to secure a good adherence of the oxide film and the cordierite support. However, we found a secondary effect of the binder, which negatively affects the catalyst selectivity. Accordingly, we have characterized this phenomenon, to gain insight about the catalytic effect of the binder.

2. Experimental

2.1. Preparation of catalysts

Table 1 lists the catalysts prepared for this study, the methodologies employed to deposit the catalytic ingredients either in powders or in preshaped structures, and the pretreatments used prior to catalytic reaction. A detailed summary of the preparation of powder and monoliths catalysts is given below.

2.1.1. Preparation of powder catalysts

2.1.1.1. Co and PtCoZSM5. Catalysts were prepared by ion exchange starting from NaZSM5 zeolite (Air Products, lot 7461-10252), unit cell $Na_9(AlO_2)_9(SiO_2)_{87}\cdot 16H_2O$). Monometallic cobalt-exchanged NaZSM5 (CoZSM5) solids were prepared using cobalt acetate solution (0.025 M). The suspension contained 7 g of zeolite per liter of solution. The exchange time was 24 h at 80 °C and then the solid was filtered, washed and dried at 120 °C for 8 h. CoZSM5 was calcined, heating at 2 °C/min in O_2 flow up to 350 °C. For the PtCoZSM5 systems, CoZSM5 was subjected to a second exchange with $Pt(NH_3)_4(NO_3)_2$ and then the sample was filtered and dried at 120 °C, for 8 h. The chemical composition of the two catalysts was 4.9 wt.% of Co for the monometallic CoZSM5, and 4.9 wt.% of Co and 0.5 wt.% of Pt for the bimetallic PtCoZSM5.

2.1.1.2. CoZSM5 + $Al(NO_3)_3$. Other two samples were prepared by deliberately adding 2 wt.% and 8 wt.% aluminum nitrate to the CoZSM5 (4.9 wt.% Co) aqueous suspension (ratio $Al_{ad}/Co = 0.5$ and 2.0, respectively). It was dried in a stove at 120 °C for 12 h and afterwards calcined in oxygen flow at 550 °C for 2 h.

Table 1
Powders and monoliths prepared

Sample	Preparation/treatment	Addition of Co and Pt to the monolith	Treatment prior to the chemical reaction
CoZSM5 powder	I.E. with Co acetate 80 °C, 24 h Dried 120 °C	–	Calcination at 350 °C
CoZSM5 + Al Powders ratio Al/Co: 0.5 and 2.0	I.E. with Co acetate $Al(NO_3)_3$ 80 °C, 24 h Dried 120 °C	–	Calcination at 550 °C
PtCoZSM5 powder	From CoZSM5 IE with $Pt(NH_3)_4(NO_3)_2$ Dried 120 °C	–	Calcination at 350 °C Reduction at 350 °C
PtCo/ZSM5-M monolith	Washcoated with NaZSM5 +2%$Al(NO_3)_3$ Calcined 550 °C	Successive Co and Pt I.E. Dried 120 °C	Calcination at 350 °C Reduction at 350 °C
Pt/CoZSM5-M monolith	Washcoated with CoZSM5 +2%$Al(NO_3)_3$ Calcined 550 °C	I.E. with Pt Dried 120 °C	Calcination at 350 °C Reduction at 350 °C
CoZSM5-M monolith	Washcoated with CoZSM5 Calcined 550 °C	–	–
PtCoZSM5-M monolith	Washcoated with CoZSM5 Calcined 550 °C	I.E. with Pt Dried 120 °C	Calcination at 350 °C Reduction at 350 °C

I.E.: ionic exchange. Suspension of zeolite in aluminum nitrate solution. The /ZSM5 nomenclature was used to indicate that the washcoat employed was NaZSM5 + $Al(NO_3)_3$. The nomenclature /CoZSM5 was used to indicate that the washcoat employed was CoZSM5 + $Al(NO_3)_3$.

2.1.2. Preparation of monolith catalysts

2.1.2.1. Washcoat of NaZSM5 + $Al(NO_3)_3$. It was performed by impregnating a suspension made up of 40 wt.% of the ZSM5 zeolite in deionized water, on a cordierite support with square-section cells with a density of 400 cells/inch^2, whose dimensions were 1 cm × 1 cm × 2 cm. Three successive dippings of the monolith in the suspension were performed to achieve the expected zeolite load (approximately 20% on dry basis). After each immersion, air was blown to eliminate the excess liquid and achieve a homogeneously thick film on the ceramic surface. It was dried in a stove at 120 °C for 12 h and afterwards calcined in oxygen flow at 550 °C for 2 h.

2.1.2.2. Incorporation of Co and Pt. The ionic exchange was achieved suspending the NaZSM5 washcoated monolith in a nitrate of tetramine platinum solution. Afterwards, a second ionic exchange was performed with the cobalt solution keeping the temperature at 80 °C. It was later dried in an oven at 120 °C.

2.1.2.3. Washcoat of Co ZSM5. An alternative route was to washcoat the CoZSM5 powder on the cordierite. The monolith impregnation was performed following a similar sequence to that of the former preparation. The monoliths washcoated with CoZSM5 were also exchanged with a platinum solution. This preparation was performed with and without the addition of the binder.

2.1.2.4. Stability of NaZSM5 coating. Experiments in airflow at high space velocity and temperature were performed to study the stability of the ZSM5 coating without binder. No weight loss due to film detachment was detected. Thus, a more vigorous treatment was carried out. The accelerated ultrasonic test, reported in the patent literature [15], was performed in order to better evaluate the washcoat adherence. The treatment originated different degrees of erosion in the various monolithic samples. The degree of erosion was measured by weighting the sample before and after the ultrasonic treatment under an atmosphere with controlled humidity and also by visualizing the surface through microscopic observations. Recently, we found that the mechanical stability is a function of the zeolite type used, the order being ZSM5 > Mordenite > Ferrierite. Even without binder, the ZSM5 washcoated monolith presented good adherence [16].

2.2. Catalytic measurements

Mono and bimetallic powder catalysts and those supported on the ceramic monolith were evaluated in a continuous flow system. Prior to the catalytic evaluation, the sample was calcined in O_2 flow at 350 °C and then reduced with H_2 at the same temperature. The typical composition of the reactant feedstream was the following: 1000 ppm NO, 1000 ppm CH_4, 2% O_2 in helium. The reaction was performed under atmospheric pressure and a temperature range between 250 and 650 °C, with GHSV = 10,000 h^{-1} (flow density of the zeolite/zeolite mass). In some runs, water (2%) was also introduced in the feed in order to test the deactivation behavior due to water vapor.

The gaseous mixtures were analyzed with an SRI 9300B chromatograph equipped with two columns, a five molecular sieve and a Chromosorb 102. The NO_x conversion (C_N) was calculated from N_2 production: $C_N = 2.100([N_2]/[NO]^\circ)$, where $[NO]^\circ$ is the NO initial concentration. The CH_4 conversion (C_{CH}) was obtained as $C_{CH_4} = 100([CH_4]^0 - [CH_4])/[CH_4]^0$.

2.3. Catalysts characterization

2.3.1. TPR experiments

These experiments were performed using an Okhura TP-2002 S instrument equipped with a TCD detector. The reducing gas was 5% H_2 in Ar, flowing at 30 mL/min and the heating rate was 10 K/min up to 900 °C.

Fresh powder samples (0.050 g), Co- and PtCoZSM5, were pre-treated in situ in flowing O_2, heating at 2 °C/min up to 350 °C and kept at that temperature for 2 h. In the case of powder samples with binder, CoZSM5 + $Al(NO_3)_3$, the calcination temperature was 550 °C. The amount used of washcoated monolith catalysts was 0.2–0.25 g, crushed into small pieces. The fresh samples were calcinated at 550 °C and the heating rate was 2 °C/min. The H_2 consumption is not referred to the cobalt content of the monolith sample (as in the case of powder samples) due to uncertainty about it.

2.3.2. Raman spectroscopy

The Raman spectra were recorded with a TRS-600-SZ-P Jasco Laser Raman instrument, equipped with a CCD (change-coupled device) with the detector cooled to about 153 K using liquid N_2. The excitation source was the 514.5 nm line of a Spectra 9000 Photometrics Ar ion laser. The laser power was set at 30 mW. For Raman spectroscopy the powder sample, calcined and used, were pressed at 4 bar into self-supporting wafers and the monolith samples were used as were prepared and after used in catalytic test.

2.3.3. X-ray diffraction (XRD)

The XRD patterns of the calcined and used solids were obtained with a XD-D1 Shimadzu instrument, using Cu Kα radiation at 35 kV and 40 mA. The scan rate was 1°/min for values between $2\theta = 5^\circ$ and 50°.

2.3.4. X-ray photoelectron spectroscopy

X-ray photoelectron spectra were acquired with an ESCALAB 200R electron spectrometer equipped with a hemispherical electron analyzer and Al Kα X-ray source ($h\nu$ = 1486.6 eV). The Si 2p, Al 2p, Co 2p, O 1s and C 1s core-level spectra were recorded for all the samples. All the peaks were fitted by a Gaussian-Lorentzian component waveform after an inelastic (Shirley-type) background had been

subtracted. In order to calculate the surface atomic ratio (n_i/n_j) the following equation was used:

$$\frac{n_i}{n_j} = \left(\frac{I_i}{I_j}\right)\left(\frac{s_j}{s_i}\right)\left(\frac{\mathrm{KE}_i}{\mathrm{KE}_j}\right)^{1/2}$$

where I is the intensity of the peak, σ is the ionization cross section and KE is the kinetic energy of the element i or j, respectively. The samples calcined and the catalysts used in the SCR reaction were dehydrated in a vacuum (10^{-5} Torr), followed by heating at a rate of 5 °C/min up to 350 °C to remove adsorbed water. Samples were also reduced in situ within the pretreatment chamber of the spectrometer under H_2 atmosphere at 400 °C for 1 h.

3. Results

3.1. Catalytic behavior

First, NaZSM5 + $Al(NO_3)_3$ was washcoated on the cordierite. After calcinations at 550 °C, both Co and Pt were exchanged onto the zeolite (PtCo/ZSM5-M). The resulting catalyst was active but unselective (Fig. 1). A second attempt was made by washcoating CoZSM5 + $Al(NO_3)_3$ and after calcinations, the Pt was introduced (Pt/CoZSM5-M). This procedure made things even worse (zero selectivity, not shown). Thirdly, the powder form of CoZSM5 was slurried with $Al(NO_3)_3$, then dried and calcined and assayed. The selectivity was again very low (Fig. 1). Note that the catalysts which included aluminum nitrate are very active for methane oxidation.

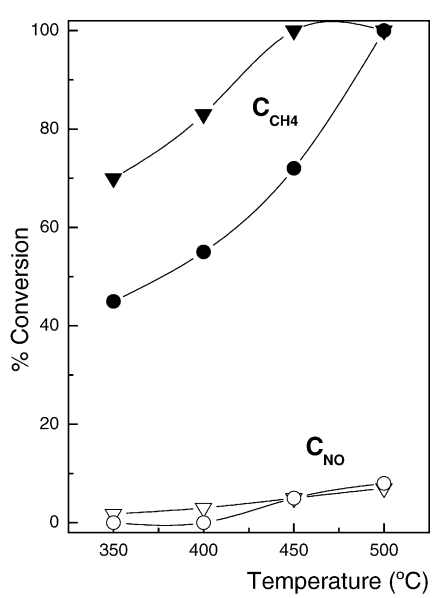


Fig. 1. Catalytic behavior in the SCR of NO with CH_4. Reaction conditions: 1000 ppm NO, 1000 ppm CH_4, 2% O_2 in He, GHSV = 10,000 h^{-1}. (▼, ▽) PtCo/ZSM5-M, washcoated with NaZSM5 + $Al(NO_3)_3$, calcined at 550 °C, then Co and Pt exchanged. (●, ○) Pt/CoZSM5, washcoated with CoZSM5 + $Al(NO_3)_3$, calcined at 550 °C, Pt exchanged.

Consequently, mono and bimetallic monolithic catalysts were prepared without binder. Fig. 2 shows that the monolith washcoated with PtCoZSM5 is somewhat better than the starting powder. It also shows that the bimetallic monolith has a better performance than the monometallic one. The same effect of Pt was reported for the powder form not only of PtCoZSM5 but also for mordenite and ferrierite [7].

After 80 h of on-stream operation and several heating-cooling cycles with or without 2% water added to the feed stream, the used Pt–Co monolith was inspected using a microscope. No deterioration of the washcoat film was observed.

3.2. TPR data

This technique may yield some clues about the cobalt distribution and location in the zeolite matrix. Fig. 3 compares the TPR profiles of calcined and used PtCoZSM5 powder with the corresponding monolith without binder after use. Note that while the profiles of the used monolith and powder are very similar, there is one order of magnitude difference between the signal intensities of monolith and powder. In the former case, the specific H_2 consumption cannot be calculated because the amount of Co in the sample is not easily quantified.

Table 2 shows the H_2 consumption from calcined and used powder catalysts. It is clear that the PtCoZSM5 powder cannot be completely reduced even after use. The high temperature peak that appears in the fresh powder seems to split in two after use. The peaks appearing below 400 °C may be due to the presence of some sort of cobalt oxides of either a different nature, a different size, or both. The lowest temperature peak should include the Pt contribution to H_2 consumption. However, the total consumption of H_2 calculated from this peak is about two times larger than the amount needed to reduce Pt^{2+} to Pt^0.

Fig. 4 hints possible causes for the loss of selectivity upon aluminum nitrate addition to the CoZSM5 suspension. First, note the qualitatively different profiles of calcined Co-ZSM5 with and without aluminum nitrate (compare traces in Fig. 4A and B). Besides, going to Table 1 one sees that only 50% of the Co^{2+} is reduced in the calcined solid while this percentage goes essentially to 100% when the aluminum salt is present in the suspension (ratio $Al_{ad}/Co = 0.5$). The sharp peak in Fig. 4B also seems to indicate that only one dominant type of reducible Co species is now present in the system (profile d). Note, however, that a second tiny bump shows up at ca. 400 °C. After use, two peaks are now visible (Fig. 4B(e)), the total H_2-consumption goes to 1.18 H_2/Co (Table 2), and the peak temperatures go down compared to the calcined solids. After increasing the amount of $Al(NO_3)_3$ added to the CoZSM5 powder to reach a $Al_{ad}/Co = 2$ ratio, the reduction maximum moves up to 780 °C. The H_2 consumption results $H_2/Co = 0.8$ (Fig. 4B(c)).

From the TPR data, it is concluded that the addition of $Al(NO_3)_3$ leads to the expulsion of the Co^{2+} cations from the

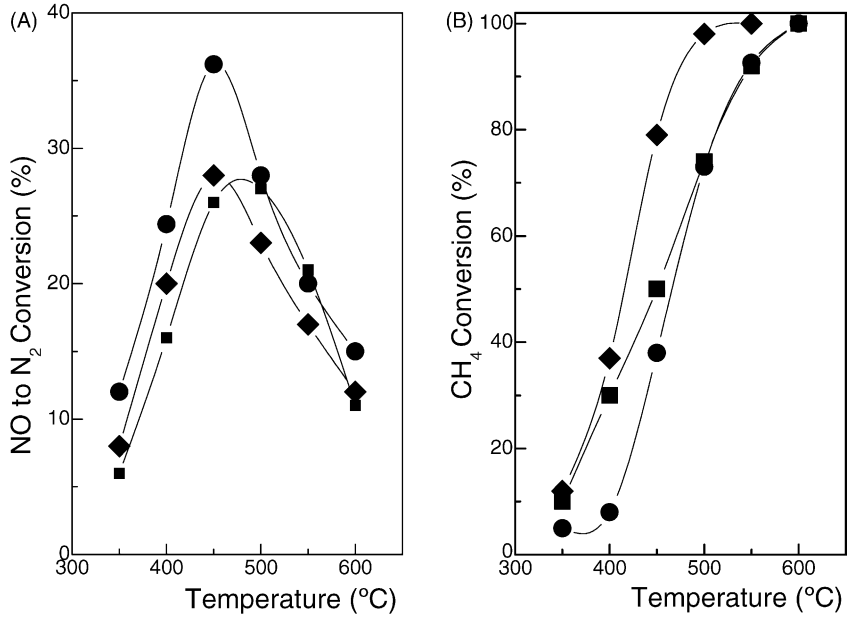


Fig. 2. Catalytic behavior in the SCR of NO with CH_4. Reaction conditions: 1000 ppm NO, 1000 ppm CH_4, 2% O_2 in He, GHSV = 10,000 h^{-1}. (A) NO to N_2 conversion. (B) CH_4 conversion. (◆) PtCoZSM5 powder, (●) Pt/CoZSM5-M, (■) CoZSM5-M.

exchange positions to form almost exclusively a cobalt-containing species that can be completely reduced at ca. 600 °C when Al_{ad}/Co = 0.5. This new species partially decomposes on stream to yield Co_3O_4 according to the peak centered at 295 °C (Table 2). This oxide is known to be active for methane combustion but unselective to N_2 production (Fig. 1).

The XRD patterns of all the solids studied only show the characteristic reflections of the zeolite matrix. In no case were the highest intensity lines of the different cobalt and mixed cobalt–aluminum oxides detected. In this search, the diffraction patterns were recorded in such a way as to increase the sensitivity of the technique. Let us see if Raman spectroscopy can help identify the nature of the species hinted by the TPR experiments.

3.3. Raman spectroscopy

In a previous study [9], we reported that used PtCoZSM5 essentially contains Co^{2+} at exchange positions plus about 40% of highly dispersed Co_xO_y species. Instead, in the case of CoZSM5, Co_3O_4 dominates the Raman spectrum, the remaining species being Co^{2+} at exchange positions. No highly dispersed Co_xO_y species are observed.

Fig. 5 shows the spectra of CoZSM5 with and without binder added. The bands at 342 and 380 cm^{-1} belong to the ZSM5 structure. The former is assigned to the bending mode of the five membered rings [17]. The two spectra at the bottom belong to the zeolite without binder, calcined and after use. The former shows no bands while the latter exhibit the characteristic signals of Co_3O_4 at 689, 520 and 480 cm^{-1}[16].

The spectrum of the calcined CoZSM5 with $Al(NO_3)_3$ (Al_{ad}/Co = 0.5) shows a dominant broad band centered at 595 cm^{-1} together with two other bands at 689 and 342 cm^{-1}. After being on stream several hours, the spinel bands develop at 689, 520 and 480 cm^{-1}. The signal at 595 cm^{-1} has been previously assigned to highly dispersed Co_xO_y [9]. On the other hand, Ohtsuka et al. [18] observed this band in Co-beta zeolite with 97% of exchanged-cobalt, which was assigned to the Co–O symmetric stretch mode of μ-oxo bridged cobalt dimerspecies, i.e. Co–O–Co.

The spectrum of the $CoAl_2O_4$ (spinel structure) shows bands at 753, 690, 619 (broad), 519, 480, 412 and 198 cm^{-1} [19]. In order to detect the possible formation of this compound, the necessary amount of $Al(NO_3)_3$ was added to the CoZSM5 suspension to reach the stoichometric ratio of the aluminate (Al_{ad}/Co = 2). The spectrum obtained after the sample was calcined at 550 °C is also shown in Fig. 5e. Note that now the bands around 755 cm^{-1} and 595 appear in the spectrum together with the others that complete the $CoAl_2O_4$ fingerprint.

The calcined PtCoZSM5 powder (Fig. 6A) shows the dispersed cobalt oxide band at 595 cm^{-1} and the main one of Co_3O_4 at 690 cm^{-1}. After being on-stream for 80 h with 2% water, the Raman spectrum shows the formation of Co_3O_4. In this catalyst, the selectivity to N_2 decayed with time on-stream while the combustion of CH_4 was favoured. This spectrum is different from the one recorded for the same catalyst after 20 h on-stream. At that time the catalyst was still selective and the only band recorded appeared at 595 cm^{-1} [9].

Fig. 6B shows the Raman spectra of the bimetallic monoliths which were prepared as indicated in Table 1. The PtCoZSM5-M, prepared from the CoZSM5 washcoat

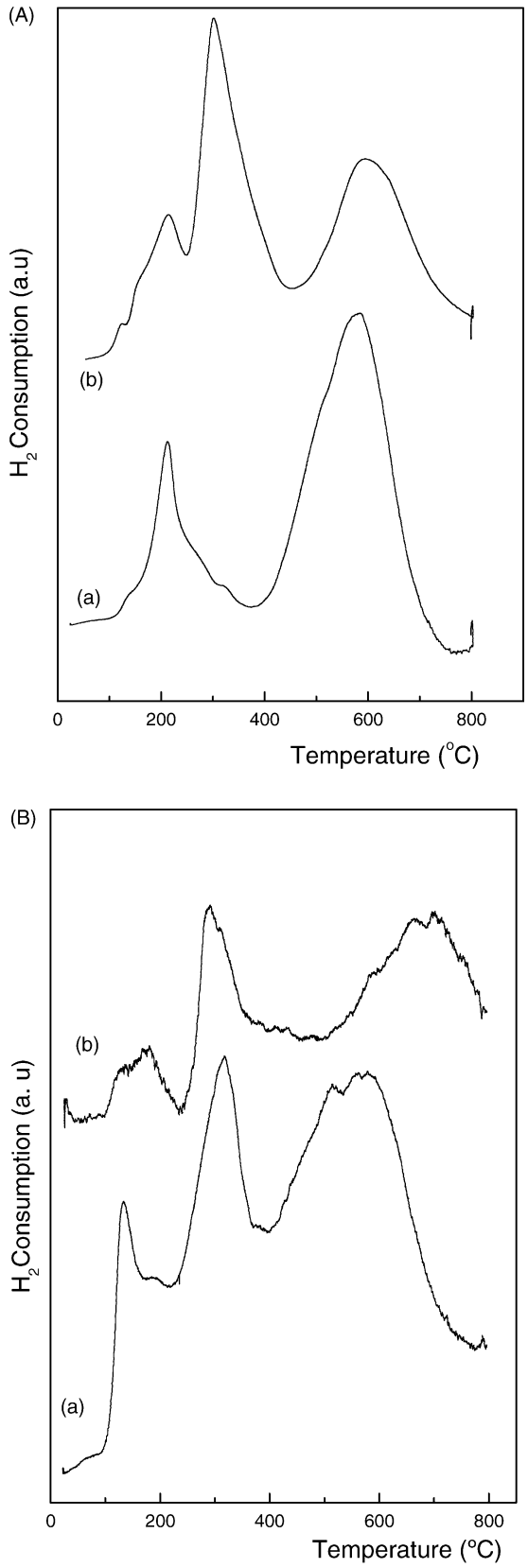


Fig. 3. TPR of (A) PtCoZSM5 powder and (B) PtCoZSM5-M; profiles (a) calcined and (b) used.

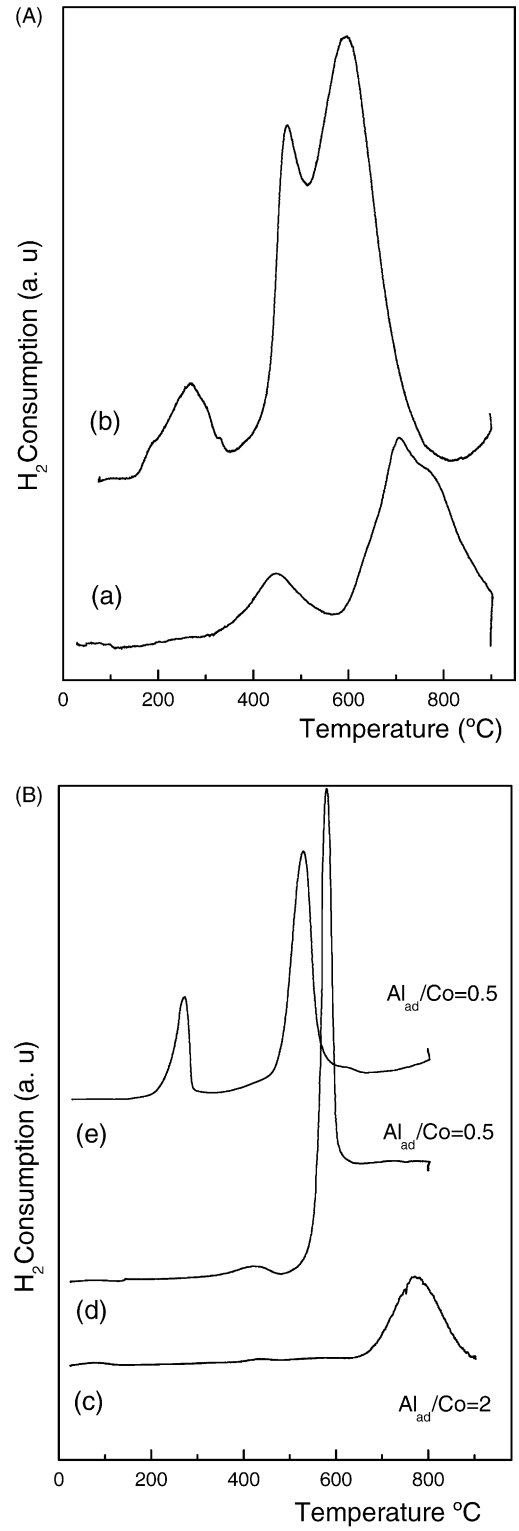


Fig. 4. TPR of CoZSM5 powder. (A) without Al $(NO_3)_3$ and (B) with $Al(NO_3)_3$; profiles (a), (c) and (d) calcined; (b) and (e) used.

without binder, was the most active for the reduction of NO_x to N_2, in the presence of H_2O. The spectrum of the calcined sample does not show any band due to the fluorescence of this solid while the used sample shows a small band at

Table 2
TPR data of Co and PtCoZSM5 (powder) and PtCoZSM5-M

Catalyst	Treatment	H_2/Co, *T* maximum (°C)		
		Peak 1	Peak 2	Peak 3
CoZSM5	Calcined	–	0.1 (450)	0.38 (710)
	Used	0.08 (270)		0.82 (595)
CoZSM5 with $Al(NO_3)_3$	Calcined (Al_{ad}/Co = 0.5)	–	0.10 (424)	0.94 (580)
	Used (Al_{ad}/Co = 0.5)	0.33 (298)		0.85 (541)
	Calcined (Al_{ad}/Co = 2.0)			0.79 (771)
PtCoZSM5	Calcined	0.12 (210)	–	0.62 (590)
	Used	0.06 (210)	0.34 (300)	0.38 (600)
PtCoZSM5-M[a]	Calcined	0.38[a]	(0.62) 511	(0.6) 620
	Used	(131–272) (0.1) 143	(0.3) 247	

[a] The (peak area/total area) ratio was used instead of the H_2/Co ratio.

690 cm^{-1} plus other two at 389 and 343 cm^{-1} belonging to the ZSM5 structure. When $Al(NO_3)_3$ was added during the washcoating of either CoZSM5 or NaZSM5, the resulting catalysts were not selective to N_2 (Fig. 2). The spectra of these powder catalysts show the characteristic bands common to both the Co_3O_4 and the cobalt aluminate (Fig. 5). The 755 cm^{-1} signal may not be seen due to the smaller amount of catalyst present in the monolithic samples.

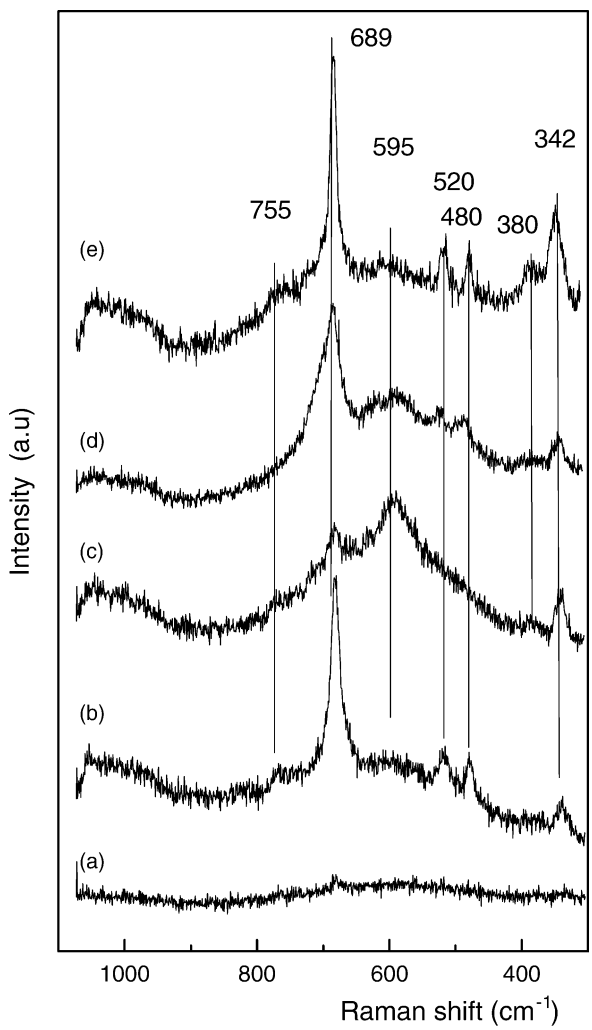
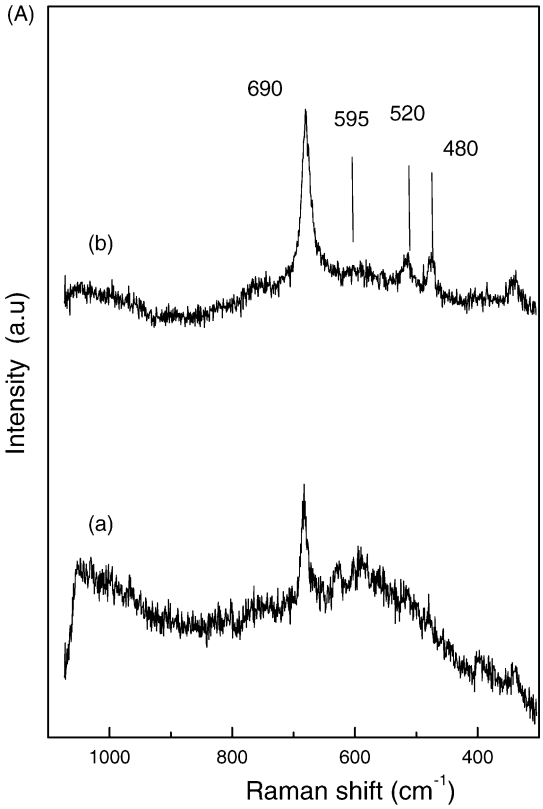


Fig. 5. Laser Raman spectra of CoZSM5 powder: (a) calcined, (b) used, (c) with $Al(NO_3)_3$ (Al_{ad}/Co = 0.5) calcined, (d) with $Al(NO_3)_3$ (Al_{ad}/Co = 0.5) used, (e) with $Al(NO_3)_3$ (Al_{ad}/Co = 2) calcined.

3.4. XPS data

Table 3 summarizes both the binding energies (BE) and the surface atomic ratios of powder samples. For the sake of clarity, Fig. 7 displays the Co 2p core-level profiles of monometallic powdered samples. The binding energy of the most intense Co $2p_{3/2}$ level varies in the 782.4–780.5 energy region depending on the catalyst pretreatment. BE values of the Co $2p_{3/2}$ level close to 782 eV correspond to Co^{2+} ions located at exchange positions of the ZSM5 zeolite [20], while those around 780 and 781 eV would be responsible for cobalt ions in a Co_3O_4 structure. From an inspection of the data collected in Table 3, it is clear that all the calcined samples show BE values of Co $2p_{3/2}$ level characteristic of Co^{2+} ions located at exchange positions, except in the two CoZSM5 + $Al(NO_3)_3$ (Al_{ad}/Co = 0.5) and CoZSM5 + $Al(NO_3)_3$ (Al_{ad}/Co = 2.0) calcined samples, in which the BE decreases from 782.4 to 781.2 and 781.8 eV, respectively, upon air-calcination up to 550 °C. It can be noted that the BEs of the Al_{ad}/Co = 0.5 and 2.0 samples, reduced in situ at 400 °C within the pretreatment chamber of the spectrometer, remain essentially unchanged.

The lower BE values of the Co $2p_{3/2}$ peak in the Al_{ad}/Co = 0.5 and 2.0 samples compared to the exchanged counterpart (CoZSM5) indicate that a cobalt aluminate phase has been formed. This finding agrees with the Raman spectra and particularly in the Al_{ad}/Co = 2.0 sample in which all the peaks of the $CoAl_2O_4$ could be identified. In both Al_{ad}/Co = 0.5 and 2.0 samples, the small variation of the BE values of Co $2p_{3/2}$ in the H_2-reduced samples precludes the involvement of a Co_3O_4 species since, if present, a shift toward lower BEs of the Co $2p_{3/2}$ peak and a simultaneous change of the shake-up satellite of Co 2p lines should appear. In addition, on looking at the Co/Si atomic ratios in Table 3, it appears that this ratio decreases slightly either in the used



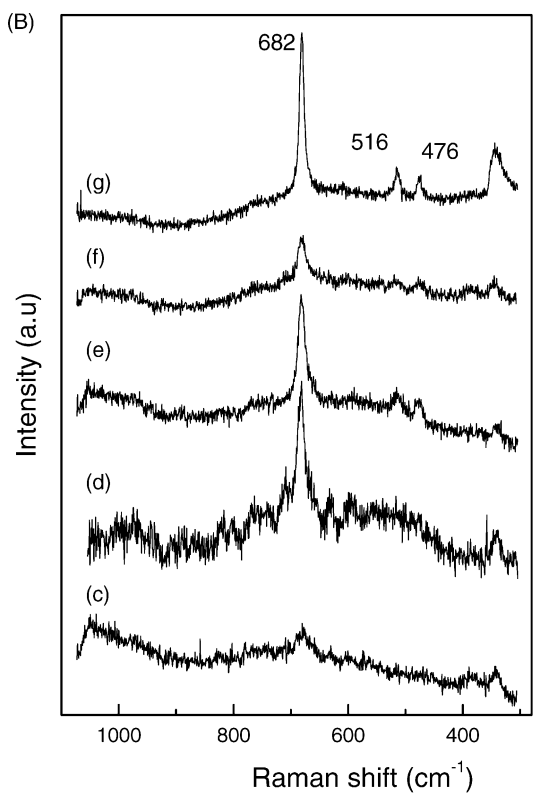


Fig. 6. Laser Raman spectra of PtCoZSM5: (A) powder and (B) monolite; (a) calcined, (b) used; (c) PtCoZSM5-M used, (d) Pt/CoZSM5-M calcined, (e) Pt/CoZSM5-M used, (f) PtCo/ZSM5-M calcined, (g) PtCo/ZSM5-M used.

Table 3
XPS data

Powders	Treatment	BE Co $2p_{3/2}$ (eV)	Co/Si[a] (0.17)[b]	Si/Al[a] (9.6)[b]
CoZSM5	Calcined	781.7	0.66	10.8
	Used	781.1	0.58	13.3
CoZSM5 + $Al(NO_3)_3$	Fresh	782.4	0.85	3.0
	Calcined	781.2	0.63	2.6
$Al_{ad}/Co = 0.5$	Used	781.2	0.48	2.7
	H_2 400 °C in situ	780.5	0.43	2.7
$Al_{ad}/Co = 2.0$	Calcined	781.9	0.32	5.3
	H_2 400 °C in situ	781.8	0.28	4.3
PtCoZSM5	Calcined	781.9	1.31	10.6
	Used	780.9	0.96	5.4

[a] Atomic surface ratios.
[b] Bulk atomic ratios.

or in the H_2-reduced samples. This would suggest some clustering of the cobalt phases as thermally induced along the reduction or on-stream operation.

Finally, the powdered bimetallic PtCoZSM5 sample shows the BE of the $Co2p_{3/2}$ at 781.9 eV, which is characteristic of Co-exchanged with the zeolite. This BE decreases to 780.9 eV, which would correspond to the cobalt oxide detected by Raman spectroscopy.

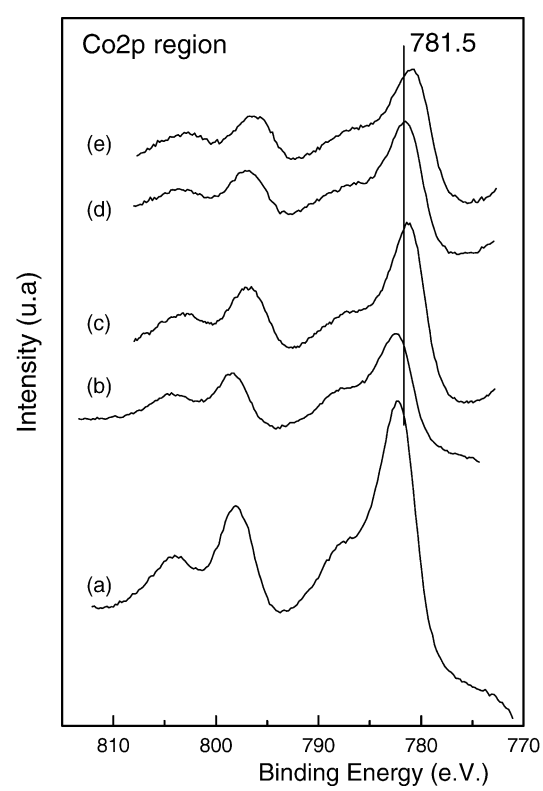


Fig. 7. XPS spectra of CoZSM5 powder: (a) calcined, (b) with $Al(NO_3)_3$ ($Al_{ad}/Co = 0.5$) fresh, (c) with $Al(NO_3)_3$ ($Al_{ad}/Co = 0.5$) calcined, (d) with $Al(NO_3)_3$ ($Al_{ad}/Co = 0.5$) used, (d) with $Al(NO_3)_3$ ($Al_{ad}/Co = 0.5$) used and reduced at 400 °C.

4. Discussion

The use of binders with zeolites to form pellets and to washcoat them to cordierite honeycomb monoliths are usually prescribed. It is acknowledged, however, that their incorporation may significantly affect the catalytic behavior of the powdered solid. In this work, we have shown that the addition of $Al(NO_3)_3$ is fatal to N_2 selectivity and in this case it was better not to use any binder.

Besides, we have understood how the binder affects the catalytic properties of the ZSM5. The TPR, Raman spectroscopy and XPS techniques all point out to the formation of $Co_{1+y}Al_{2-x}O_4$ which, while on stream partially decomposes to form small amounts of Co_3O_4 (Table 3). This oxide is an active oxidation catalyst but unselective towards N_2 formation. The TPR profiles of the solids recovered from the suspension containing $Al(NO_3)_3$ in different proportions and then calcined at 550 °C exhibit single reduction peaks at 580 and 780 °C. The former corresponds to $Al_{ad}/Co = 0.5$ and the latter to $Al_{ad}/Co = 2.0$. These profiles are completely different from those observed with either powders or washcoated monoliths without aluminium nitrate added (compare Fig. 4B with Figs. 4A and 3). Moreover, this displacement of the reduction peak to higher temperatures with increasing addition of $Al(NO_3)_3$ is consistent with the formation of harder to reduce, more stoichiometric spinel structures. The Raman fingerprint of the cobalt aluminate shown in the spectrum of Fig. 5 is key to the identification of this compound.

The XPS data also support the presence of a cobalt aluminate on the surface of the solids resulting from the interaction between the catalyst and $Al(NO_3)_3$. Table 3 shows that the $Co2p_{3/2}$ BE for the fresh solid is 782.4 eV but after calcinations it goes down to 781.8 eV for $Al_{ad}/Co = 2.0$ and 781.2 eV for $Al_{ad}/Co = 0.5$. This is symptomatic of the fact that the Co^{2+} originally located at exchange positions reacted with aluminium retained by the solid during calcinations at 550 °C to form $CoAl_yO_x$ species. These surface species cannot be reduced in H_2 at 400 °C, since there are neither changes in BEs (Table 3) nor is the satellite peak affected (Fig. 7). This is also confirmed by the bulk TPR data that shows that H_2 consumption at $T = 420$ °C is less than 10% of the total. Thormählen et al. [21] identified through XPS and XRD a cobalt aluminate spinel $Co_{1.66}Al_{1.34}O_4$ (containing Co^{2+} and Co^{3+}) that they could distinguish from both Co_3O_4 and $CoAl_2O_4$. Our Raman data confirm the assignments we made above.

Fig. 2 shows that the selective washcoated monolith was obtained without using any binder. Furthermore, it was hydrothermically stable. This was possible because the NaZSM5 that we used has a small average particle size of 5 μm. When we tried to do the same with ferrierite with a particle size of 90 μm, the washcoat was not durable. To solve the adherence problem, we used aerogel silica as binder which did not affect the catalytic behavior of the powder [14].

5. Conclusions

The washcoating of ZSM5 with an average particle size of 5 μm can be successfully done without the use of binders. The resulting catalyst was as good as the starting powder.

When $Al(NO_3)_3$ was used as binder, it reacted with the exchanged cobalt ions during calcinations at 550 °C to form a non-stoichiometric spinel, $Co_{1+y}Al_{2-x}O_4$. Under reaction conditions, this compound partially decomposes to yield Co_3O_4 which acts as a good combustion catalyst.

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