The beneficial effect of silica on the activity and thermal stability of PtCoFerrierite-washcoated cordierite monoliths for the SCR of NO$_x$ with CH$_4$

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Abstract

PtCoFerrierite washcoated on a ceramic monolith is an active and selective catalyst for the SCR of NO$_x$ with methane. For our system, we found that the addition of a binder to the slurry used for the washcoat is necessary to improve the adherence and to obtain a selective catalyst. In our case, we used 2 wt.% of Cabot Silica. Ultrasound experiments used to comparatively evaluate the coating adherence showed that silica prevents the washcoat loss due to attrition. Similar monolithic catalysts, but prepared without a binder, resulted in catalysts with poor activity for NO$_x$ reduction, but still active for the deep oxidation of methane with oxygen. Monoliths washcoated without a binder showed both Pt segregation to the outer surface of zeolite crystals and formation of the non-selective Co$_3$O$_4$. Segregated Pt clusters and cobalt oxide promote the methane combustion with oxygen, thus leaving the NO$_x$ molecules unreacted. Moreover, due to Pt segregation, the necessary intimate contact between Pt and Co active species is not favored in this catalyst, which also contributes to the low selectivity to N$_2$.
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Keywords: SCR of NO$_x$; Zeolite; Zeolite washcoated monoliths; NO$_x$ + CH$_4$

1. Introduction

The proven technological options available to abate NO$_x$ emissions from combustion gases are essentially two. In the case of Otto-cycle engines, three-way catalysts are very effective as long as the engine operates close to the stoichiometric air/gasoline ratio [1]. To deal with NO$_x$ emissions from stationary sources, the reduction with ammonia using either V$_2$O$_5$/TiO$_2$ [2] or metal-zeolites [3] is the route of choice. The use of ammonia, itself a toxic, corrosive gas, increases both the initial investment and the cost of operation.

This is why there is a great deal of activity trying to find a more friendly reductant. Methane is the right candidate because this gas is readily available at most power stations.

Starting with the pioneering works of Iwamoto [4] and Held et al. [5], a long list of publications has appeared in the open literature concerning the use of metal-exchanged zeolites to selectively reduce NO$_x$ with different hydrocarbons and particularly with methane [6]. In the last few years, the combination of different active materials using two or more catalytic beds [7] and the use of bimetallic zeolites have improved the water resistance of these systems [8]. Kikuchi and co-workers studied Pt–In, Ir–In, and Pd–Co exchanged ZSM5 [9–11]. Pd–Co in mordenites

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was also studied by Bustamante et al. [12]. Our group worked with Pt–Co in mordenites, ZSM5 and ferrierites [13–15]. In most cases the addition of the noble metal significantly increases the resistance to water deactivation of the zeolite formulations.

The great majority of these studies were performed in microreactors using powder catalysts. However, for practical applications these catalysts should be shaped as honeycomb monoliths. There are three ways of doing so: (i) massive extruded zeolite monoliths [16], (ii) zeolite films grown on top of cordierite [17], and (iii) zeolite powder washcoated on cordierite [18].

Only a few articles concerning the selective catalytic reduction of NO_x with methane using monoliths have been published. Among them, the ones by Heinisch et al. [19], Bahamonde et al. [20], and Bustamante et al. [12] are particularly pertinent to these studies. The first one reported 70% conversion of NO to N_2 at 400 °C (no water added) using a massive ZSM-5 monolith exchanged with Pd and In. Bahamonde et al. [20] employed monolithic catalysts based on pillared clay and zirconia in the SCR of NO_x with methane. In that work, they reported that good selectivity results were obtained only through the use of a high CH_4/NO ratio.

We have chosen to washcoat ferrierite powder on cordierite and use these monoliths to react NO_x with CH_4 in the presence of excess oxygen with and without added water. The main goal of this study was to find out a good preparation route to obtain a mechanically stable washcoated cordierite monolith with activity at least as good as the starting powder. Powder and washcoated catalysts, both fresh and used, were characterized by TPR and XPS. The adhesion of the washcoat was evaluated using an ultrasonic technique [21,22].

2. Experimental

2.1. Preparation of Co and PtCoFerrierite unsupported catalysts

Catalysts were prepared by ionic exchange starting from KFerrierite Tosoh HSZ-720KOA, unit cell $(Na, K)_{3.7}(AlO_2)_{3.7}(SiO_2)_{23.3} \cdot 10\ H_2O$ (BET area = $170\ m^2/g$). Monometallic cobalt-exchanged KFer-

rierite (CoFer) solids were prepared using cobalt acetate solution. The exchange time was 24 h at 353 K and then the solids were filtered, washed and dried at 393 K for 8 h. CoFer was calcined, heating at 2 K/min in O_2 flow up to 673 K with three isothermal legs, at 383 and 483 K for 2 h each, and at 673 K for 8 h. The PtCoFer systems were prepared by successive exchanges. First the KFer was exchanged with cobalt acetate and dried at 393 K. Then, the CoFer was subjected to a second exchange with $Pt(NH_3)_4(NO_3)_2$. The sample was calcined in O_2 at slow heating rate (0.5 K/min, up to 623 K) and then reduced with flowing H_2 for 1 h at 623 K. Another bimetallic sample was calcined at 823 K and then reduced at 623 K. The calcined and used samples showed no significant changes in the BET area.

2.2. Preparation of washcoated monolithic catalysts

2.2.1. Washcoat with CoFerrierite

A suspension with 40 wt.% of CoFer (in deionized water) was used to impregnate a cordierite support (Corning) having square-section cells with a density of 400 cells/in^2. Successive immersions of the monolith in the suspension were performed to achieve the expected zeolite load (approximately 20 wt.% on a dry basis). After each immersion, air was softly blown to eliminate the excess suspension to achieve a homogeneously thick film on the ceramic surface. It was dried at 393 K for 12 h in horizontal position and afterwards calcined in oxygen flow at 823 K for 2 h. Selected samples of washcoated monoliths were photographed using a Nikon FX-35-DX microscope. The observation of these pictures indicates that the catalysts were homogeneously deposited on the monolith walls.

2.2.2. Washcoat with PtCoFerrierite
It was prepared in two ways:

(i) Through ionic exchange from a platinum solution $((Pt(NH_3)_4(NO_3)_2)$ in which the monolith washcoated with CoFerrierite was suspended for 24 h at room temperature.
(ii) Using the PtCoFer powder, the monolith impregnation was done following a similar sequence to that of the former preparation (Section 2.2.1).

This preparation was performed with or without the addition of a binder. (CAB-O-SIL, surface area = 200 m^2/g; particle diameter = 5–30 nm). The washcoated monolith was calcined heating at 0.5 K/min in O$_2$ flow up to 823 K in order to obtain a good adherence of the zeolite crystals to the monolith walls. It was then reduced with flowing H$_2$ for 1 h at 623 K.

2.3. 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 monometallic samples were calcined only in O$_2$ flow while the bimetallic solids were first calcined in O$_2$ and then reduced in H$_2$ at 623 K [13]. The typical composition of the reacting stream was the following: 1000 ppm NO, 1000 ppm CH$_4$, 2% O$_2$ in helium. The reaction was performed under atmospheric pressure at temperatures between 523 and 923 K, with different flow/catalyst weight ratios $(F/W) = (GHSV)/\rho$, where ρ (powder density, ca. 0.5). The washcoated monoliths (1 cm × 1 cm × 2 cm) were placed in the same reactor between two quartz wool plugs. In some runs, water (2–10%) was also introduced in the feed in order to test the deactivation behavior of the best formulations.

The gaseous mixtures were analyzed with an SRI 9300B chromatograph equipped with two columns, a 5 Å molecular sieve and a Chromosorb 102. The NO$_x$ conversion (C$_{NO}$) was calculated from N$_2$ production: $C_{NO} = 2 \times 100([N_2]/[NO]^0)$, where $[NO]^0$ is the initial concentration of NO. In a few selected experiments the nitrogen balance was checked through the measurement of NO$_x$ concentrations using the infrared absorption bands of NO and NO$_2$. NO and N$_2$O was never detected in the experiments reported here. The CH$_4$ conversion was obtained as $C_{CH_4} = 100([CH_4]^0 - [CH_4])/[CH_4]^0$.

2.4. TPR experiments

These experiments were performed with 100–200 mg of catalyst 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.

2.5. Surface analysis by XPS

X-ray photoelectron spectra were acquired with an ESCA 750 electron spectrometer equipped with an Al Kα X-ray source ($h\nu$ = 1486.6 eV). The Si 2p, Al 2p, Pt 4f, Co 2p, O 1s, K 2p, Al 2s, 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. For the Al 2p and Pt 4f signals the situation was more complex because they overlapped. In order to analyze the contribution of the two elements, it was assumed that the spin–orbit splitting for Pt was fixed at 3.35 eV and the Pt 4f$_{5/2}$/Pt 4f$_{7/2}$ intensity ratio was kept constant (0.75). In the case of Co 2p, the spin–orbit separation was equal to 16 eV and the 2p$_{1/2}$/2p$_{3/2}$ ratio was 0.5. Prior to the XPS measurement, fresh and used samples were dehydrated in the pretreatment chamber (10^{-5} Torr).

2.6. Washcoating adherence

The adherence of the KFerrierite coatings was evaluated using a method described by Yasaki et al. [21] in the patent literature which consists in the measurement of the weight loss caused by exposure to ultrasound. This method was recently applied by Valentini et al. [22] for alumina layers on ceramic and metallic monolithic supports. In this work, the coated monoliths were immersed in acetone inside a Pyrex vessel and then kept in an ultrasound bath for 1 h. After that, the sample was dried during 2 h at 393 K. The weight of the sample was measured under a controlled atmosphere (295 K and 80% of humidity) both after and before the ultrasonic treatment. This method was employed to comparatively measure changes in the washcoating adherence when silica was used as a binder.

3. Results

3.1. Catalysts prepared

Table 1 indicates the routes followed to obtain the exchanged ferrierite powders and the washcoated monoliths. The bimetallic supported catalysts were prepared by: (i) first washcoating CoFer and then exchanging the Pt salt (Pt/CoFer-M) or (ii) directly

Table 1
Unsupported and monolith-washcoated Co and PtCoFerrierite[a]

Sample	% Wc[b]	% Pt	Preparation	Calcination in O_2	H_2 reduction at 623 K before use
CoFer powder	–	–	Ionic exchange of KFer with cobalt acetate for 24 h at 80 °C	673 K, 2 h, 2 K/min	–
PtCoFer powder	–	0.5	CoFer exchanged with $Pt(NH_3)_4$ $(NO_3)_2$	623 K, 2 h, 0.5 K/min	Yes
PtCoFer powder	–	0.5	CoFer exchanged with $Pt(NH_3)_4$ $(NO_3)_2$	823 K, 2 h, 0.5 K/min	Yes
PtCoFer + SiO_2 powder	–	0.5	Slurry of PtCoFer + 2% SiO_2	823 K, 2 h, 0.5 K/min	Yes
CoFer-M	14	–	Washcoated CoFer	823 K, 4 h, 2 K/min	–
Pt/CoFer-M	13	0.5	Calcined CoFer-M exchanged with Pt salt	623 K, 2 h, 0.5 K/min	Yes
PtCoFer-M	20	0.5	Washcoated PtCoFer	823 K, 2 h, 2 K/min	Yes
(PtCoFer + SiO_2)-M	12	0.5	Washcoated PtCoFer + 2% SiO_2	823 K, 2 h, 2 K/min	Yes

[a] All the bimetallic ferrierites were prepared from CoFer containing 4.3% Co and Si/Al = 6.3.

[b] Indicates percentage of weight gain after washcoating the cordierite.

washcoating the PtCoFer (PtCoFer-M). In the second option, a binder (SiO_2) was used in one of the preparations (PtCoFer + SiO_2-M) (last row in Table 1).

The different calcination strategies are mainly a consequence of the required temperatures and heating rates dictated by the nature of the exchanged species [13] and the mechanical stability of the washcoat. To dehydrate and decompose the cobalt acetate exchanged powder, the solid was slowly heated up to 673 K. To decompose the Pt complex, the heating rate was four times slower and the maximum temperature kept at 623 K. In this way, the migration of Pt outside the zeolite channels was minimized. Both the monometallic and bimetallic powders washcoated to the cordierite were calcined at 823 K to firmly secure the zeolite film to the monolith surface.

3.2. Catalytic behavior

Fig. 1 compares the catalytic behavior of the bimetallic powder, taken as our reference with three different washcoated ferrierites. Note that none of them reach the powder performance. The monolith washcoated with CoFer showed a maximum NO to N_2 conversion of 17%, similar to the one observed for unsupported CoFer. When the CoFer was first washcoated onto the cordierite and then exchanged with the Pt salt, no improvement of the catalytic performance occurred. Even more surprising was the lack of N_2 production when the bimetallic powder was directly attached to the cordierite. On the other hand, high methane conversions were obtained (not shown) thus concluding that the low NO_x conversion is due to

the low selectivity of these washcoated catalysts. The PtCoFer powder calcined at 823 K (same temperature as PtCoFer-M) did not show activity for the NO to N_2 reduction, but it did show a high CH_4 conversion.

When 2% high surface area SiO_2 (acting as a binder) was added to the PtCoFer suspension, the washcoated catalysts behaved so well as the starting powder, as shown in Fig. 2. In this case the effects of water and
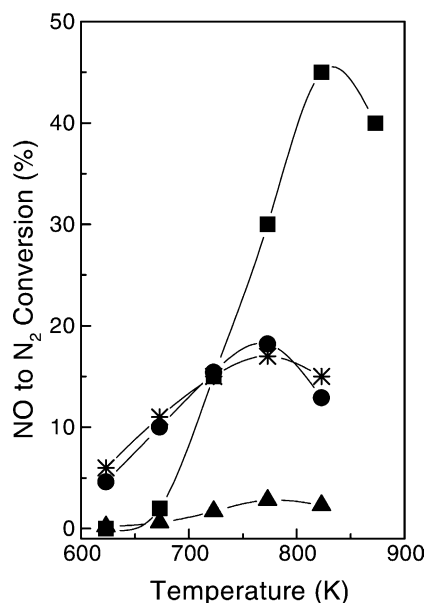

Fig. 1. Catalytic behavior of Co and PtCoFerrierite. Reaction conditions: 1000 ppm NO, 1000 ppm CH_4, 2% O_2 in He, GHSV = 20,000 h^{-1}. (■): PtCoFer powder catalyst; (●): monolith washcoated with CoFer; (∗): Pt exchanged on monolith washcoated with CoFer; (▲): monolith washcoated with PtCoFer.
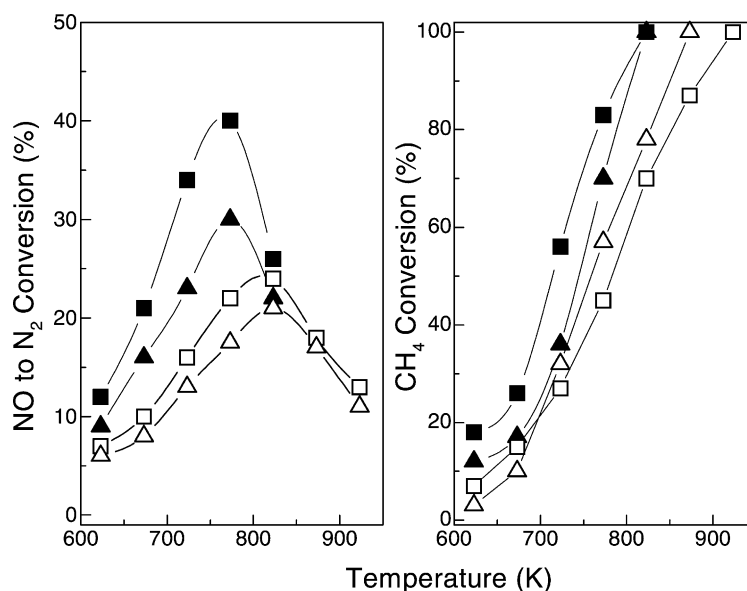
Fig. 2. Catalytic behavior of PtCoFer-monolith with SiO$_2$ addition. Reaction conditions: see Fig. 1. (■, □): GHSV = 20,000 h^{-1}; (▲, △): GHSV = 30,000 h^{-1}. Full symbols: without water; empty symbols = 2% H$_2$O.

space velocities were also explored. When 2% of water was added to the feed, only a moderate loss in NO$_x$ conversion took place. However, under more severe conditions (10% of water), the activity loss was considerably higher (not shown). For example, for GHSV = 20,000 h^{-1} the maximum NO$_x$ conversion dropped from 40 to 15% and the corresponding temperature increased from 773 to 823 K.

Table 2 shows the effect of the calcination temperature prior to reduction at 623 K. It can be observed that, when the PtCoFer powder sample is calcined at 823 K, the NO$_x$ conversion is practically null, the methane conversion being 100%. The same powder sample, but mixed with SiO$_2$ in a slurry (under the conditions used for the washcoating procedure) shows a smaller drop in conversion, being 22 and 20% for calcinations at 823 and 973 K, respectively.

In the case of washcoated monoliths, the calcination temperature must be 823 K or higher in order to get a good coating adherence. The PtCoFer-M calcined at 823 K is unselective. However, for the (PtCoFer + SiO$_2$)-M, an acceptable selectivity is retained even after calcination at 973 K.

The stability of (PtCoFer + SiO$_2$)-M was tested in long-term runs. When no water was added and the

reaction temperature was kept at 773 K, the catalytic performance remained constant after 100 h on stream. When 2% water was fed in the reacting mixture the NO$_x$ conversion initially dropped to 23% (Fig. 2). This conversion did not change much after 100 h on stream. At this point, the water saturator was bypassed and the initial conversion of NO was restored (40%).

Table 2
Effect of calcination temperature on catalytic behavior[a]

Catalysts[b]	Calcination temperature (K)	% X_{NO} max[c]	T_{max} (K)[d]
PtCoFer powder	623	45	823
	823	0	–
PtCoFer + SiO$_2$ powder	623	45	723
	823	22	773
	973	20	823
PtCoFer-M	823	2	773
(PtCoFer + SiO$_2$)-M	823	40	773
	973	20	823

[a] Reaction conditions: 1000 ppm NO, 1000 ppm CH$_4$, 2% O$_2$ in He, GHSV = 20,000 h^{-1}.

[b] After calcinations, the samples were reduced by H$_2$ at 623 K.

[c] Maximum NO to N$_2$ conversion, in all cases CH$_4$ was 100%.

[d] Temperature of the maximum NO to N$_2$ conversion.

However, under more severe conditions, 10% of water in the feedstream, the catalytic performance was irreversibly affected after 20 h on stream. In fact, the NO_x conversion, which initially dropped from 40 to 15%, decayed an additional 50% after 20 h on stream. This deactivation was now irreversible because after bypassing the saturator and waiting several hours, the NO_x conversion stayed at 5% while the CH_4 conversion reached 100%.

3.3. TPR data

When cobalt is exchanged in zeolites, different species can be generated at the solid surface, depending on the exchange procedure and on the pretreatment of the sample. Cations at exchange positions, Co_3O_4 small crystals and highly dispersed non-crystalline Co oxide species are reported in the literature as the main observable species on various zeolites. Among these, Co at exchange positions are responsible for the activity in the SCR of NO_x with methane, Co_3O_4 is a non-selective species, and non-crystalline Co oxides may help in the NO to NO_2 oxidation [23,24]. In the TPR experiments, the hardest species to reduce are the exchanged Co^{2+} (highest temperature peak) while the lowest temperature peaks are assigned to different types of cobalt oxides with varying size and strength of interaction with the lattice.

Table 3 shows the H_2/Co consumption of the metal-exchanged ferrierite powders. In most cases this ratio is lower than the unity, except for the used

bimetallic catalyst which is somewhat higher. Fig. 3 shows the TPR profiles of the powder samples CoFer and PtCoFer, calcined (Fig. 3A) and used (Fig. 3B). The CoFer calcined at 673 K shows two peaks centered at 507 and 893 K (Fig. 3A, profile a). The first one is characteristic of cobalt oxides [24] while the latter indicates that at least 65% of the Co ions are located at exchange positions in the ferrierite lattice. Note that total reduction is less than 1 H_2/Co and this indicates that not all the exchanged Co^{2+} is reduced. The incorporation of 0.5% of Pt decreases the temperature at which exchanged Co^{2+} species are reduced (highest temperature peak). The TPR of the sample calcined at 623 K exhibits a peak at 432 K and a smaller one at 554 K (Fig. 3A, profile b). From the H_2 consumption (Table 3) it is concluded that these peaks include the reduction of all the Pt^{2+} plus 29% of the total cobalt. Note that the b–d profiles are similar. However, the total H_2 consumption goes down from b to d and the lowest temperature peak almost disappears in c and d (Table 3).

Fig. 3B shows the TPR of used samples. These data provide more information concerning the effect of SiO_2 addition. CoFer and PtCoFer, calcined at 623 K and after being used, exhibit a third peak centered at 600 K which belongs to the Co_xO_y highly dispersed cobalt oxides (Fig. 3B, profiles a and b). However, a drastic change was observed when the bimetallic sample was calcined at 823 K before the reduction treatment (Fig. 3B, profile c). Remember that this solid is non-selective (Table 2). A very intense peak now

Table 3
Reducibility of Co and PtCoFerrierite powder[a]

Sample	Pretreatment	Calcination temperature (K)[b]	H_2/Co (T_{max})		
CoFer	Calcined[b]	673		0.13 (507)	0.65 (893)
	Used[c]	673		0.25 (585)	0.60 (864)
PtCoFer	Calcined[b]	623	0.29 (432–554)		0.53 (752)
	Calcined[b]	823	0.16 (425)		0.35 (756)
	Used[d]	623	0.20 (400)	0.28 (600)	0.72 (855)
	Used[d]	823	0.84 (400)	0.42 (550)	
PtCoFer + SiO_2	Calcined[b]	823	0.10 (471)		0.35 (834)
	Used[d]	973	0.73 (550)		0.43 (895)

[a] 5% H_2 in Ar, 30 ml/min, heating rate = 10 K/min up to 1073 K.

[b] Prior to TPR, the sample was calcined in situ for 2 h at calcination temperature.

[c] Prior to TPR, the sample was used at reaction conditions.

[d] Before reaction, the sample was calcined (at calcination temperature) and reduced at 623 K.
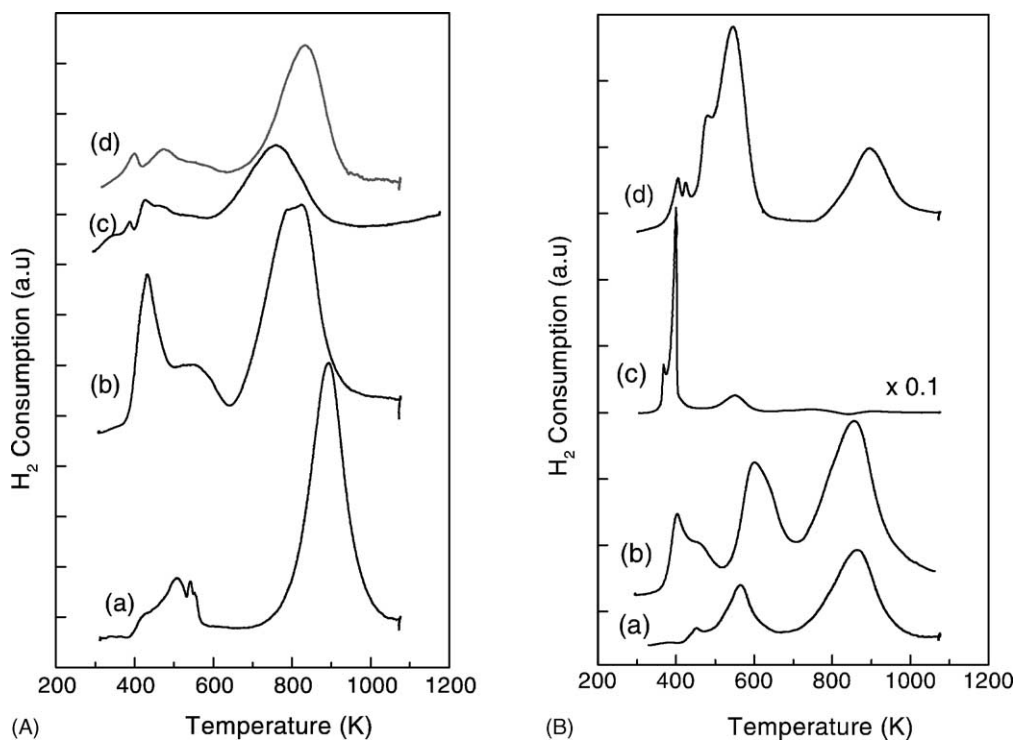
Fig. 3. TPR of Co and PtCoFer powder, 5% H_2 in Ar, 30 ml/min, heating rate 10 K/min. (A) calcined and (B) used. (a) CoFer calcined at 673 K; (b) and (c) PtCoFer, calcined at 623 and 823 K, respectively; (d) PtCoFer + SiO_2, calcined at 823 K.

appears at 400 K followed by a smaller one at 550 K. Assuming that only Co^{2+} is present in this solid calcined at 823 K, 80% of the total cobalt and all the platinum has been reduced at this very low temperature. In the same Fig. 3B, profile (d) shows the TPR for the used (CoPtFer + SiO_2) powder. Even when calcined at higher temperature (973 K), this sample retains most

of the features of the active solids, the main difference being the somewhat lower (Co^{2+})/(Co oxides) ratio.

Table 4 and Fig. 4 show the TPR data obtained for the washcoated monoliths, calcined (Fig. 4A) and used (Fig. 4B). The data presented in the table are in the form of H_2 consumption percent of each peak. They are not referred to the Co content of the sample (as

Table 4
Reducibility of washcoated Co and PtCoFerrierite[a]

Sample	Pretreatment[b]	(T_{max}) (peak area/total area)		
CoFer-M	Used	573 (0.17)		946 (0.83)
Pt/CoFer-M	Calcined	405 (0.16)	682 (0.34)	829 (0.50)
	Used	481/550 (0.69)		806/884 (0.31)
PtCoFer-M	Calcined	523 (0.19)	633 (0.19)	894 (0.62)
	Used	439/569 (0.48)		833 (0.52)
(PtCoFer + SiO_2)-M	Calcined	434 (0.24)		770 (0.76)
	Used	393/539 (0.45)		841 (0.53)

[a] 5% H_2 in Ar, 30 ml/min, heating rate = 10 K/min up to 1073 K.
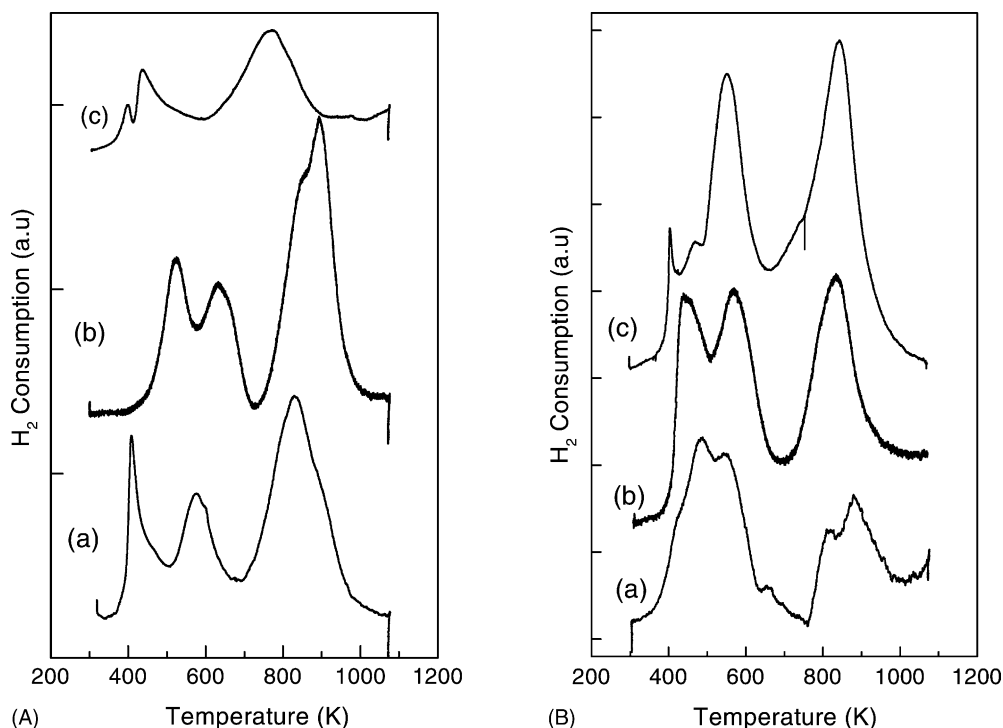[b] See conditions in Table 1.

Fig. 4. TPR of PtCoFer monolith: (A) calcined and (B) used. (a) Pt/CoFer-M; (b) PtCoFer-M; (c) (PtCoFer + SiO$_2$)-M.

in the case of powder samples) due to the uncertainty about the Co content of monolithic samples. The TPR profile of the used monometallic monolith CoFer-M (not shown) is similar to that of the calcined CoFer powder. The profiles of the fresh bimetallic monolith are essentially very similar showing at least three consumption peaks (Fig. 4A). When the washcoated CoFer calcined at 823 K is exchanged with Pt, the peak maxima appear at lower temperatures than in the case of PtCoFer-M (Fig. 4A, profiles a and b). A similar effect is observed for the (PtCoFer + SiO$_2$)-M sample. After being on stream, the TPR profile of Pt/CoFer-M is significantly modified (Fig. 4B, profile a). Now, a very wide peak appears between 400 and 600 K and another one at 750–950 K. Table 4 tells us that 69% of the H$_2$ consumption occurs at the lowest temperatures. The used PtCoFer-M shows a displacement of the maxima towards lower temperatures (Fig. 4B, profile b), compared with the calcined catalyst (Fig. 4A, profile b).

A different behavior is observed when SiO$_2$ is added during the preparation of the bimetallic mono-lith (PtCoFer + SiO$_2$)-M. The used monoliths without SiO$_2$ (Fig. 4B, profiles a and b) show a significant amount of cobalt species reducible between 400 and 500 K, assigned to Co$_3$O$_4$. The peak at 400 K disappeared when SiO$_2$ was added (profile c), showing mainly the peaks that correspond to exchanged Co^{2+} and Co$_x$O$_y$.

3.4. XPS data

Table 5 shows the data obtained with washcoated CoFer both calcined and used together with the original KFer powder. Note the constancy of both the Al 2p and Si 2p binding energies. They are coincident with data reported in the literature [25]. The K 2p$_{3/2}$ BE oscillates around 294.4 ± 0.3 eV. The BE of the Co 2p$_{3/2}$ is 782.7 eV typical of Co^{2+} located at exchange lattice positions [26–28].

Table 6 shows the XPS data obtained with bimetallic formulations calcined and used in powder form and washcoated with or without a binder (SiO$_2$). The Co 2p$_{3/2}$ BEs vary between 782 and 783 eV, while Al 2p,

Table 5
Surface features of washcoated CoFerrierite

Sample	Binding energy (eV)[a] (FWHM)				Surface atomic ratio		
	Co $2p_{3/2}$	Al 2p	Si 2p	K $2p_{3/2}$	Co/Al [0.4][b]	Si/Al [6.3][b]	K/Si [0.03][b]
Fresh CoFer-M	782.7 (3.9)	74.0 (2.3)	102.9 (2.7)	294.6 (3.1)	1.3	5.6	0.07
Used CoFer-M	781.3 (3.6)	74.0 (2.2)	102.9 (2.5)	294.1 (2.2)	1.3	5.8	0.06
KFer (starting powder)	–	74.0 (1.9)	102.9 (2.0)	294.2 (2.1)		6.2 [6.3][b]	0.07 [0.16][b]

[a] The binding energies are referenced to the C 1s peak (284.6 eV).

[b] Bulk atomic ratio.

Si 2p, and K 2p have values similar to that of Table 5. The calcined PtCoFer powder was reduced with H_2 at 623 K in the pretreatment chamber of the ESCA spectrometer. Beside the peak at 782.9 eV which corresponded to Co^{2+} ions at exchange positions, two small peaks at 780.2 and 778.7 eV were observed (Table 6), which can be assigned to Co oxide species [27].

The Pt 4f signal partially overlaps the Al 2p peak. To separate both contributions, the Al 2p intensity was calculated from the Si 2p/Al 2s ratio. After use, both PtCoFer in powder form and the monolith washcoated with SiO_2 exhibit a narrow single peak located at ca. 71.8 eV which can be safely assigned to Pt^0. On the other hand, the fresh PtCoFer prepared without a binder yields a wider Pt 4f signal which can be separated into two contributions (73.5 and 71.4 eV). In the catalysts, both metallic and cationic Pt seem to be present on the surface. After use, a single signal at 72.2 eV is observed which is similar to that prepared with a binder. Vedrine et al. [29] reported BE values between 72.8 and 71.5 in Pt^0 particles of different sizes dispersed in NaYZeolite.

A key piece of information is the migration of Pt to the ferrierite crystal external surface observed in the fresh and used washcoated PtCoFer without SiO_2. The Pt/Si surface ratio is three times higher than in the case where the binder was used or in the starting powder. Also, note that in the latter case the Pt/Si ratio is coincident with the bulk ratio calculated from the chemical analysis. It should be noted that the Pt/Si ratio of the fresh-calcined at 623 K PtCoFer is also high, but after use, the ratio sharply decreases. A similar behavior is observed for the (PtCoFer + SiO_2)-M sample. Note that both samples are selective for N_2 production.

3.5. Coating adherence

Under practical conditions, washcoated monolithic catalysts are subjected to high gaseous flow rates and

Table 6
Surface features of bimetallic catalysts[a]

Catalyst	Binding energy (eV) (FWHM)		Surface atomic ratio		
	Co $2p_{3/2}$	Pt $4f_{7/2}$	Co/Al [0.38][b]	Pt/Si [0.002][b]	Si/Al [6.3][b]
PtCoFer (calcined powder)	781.8 (3.9)	71.8 (2.2)	1.17	0.005	6.9
PtCoFer (reduced powder)	782 9 (3.3) 780.2, 17% (2.6) 778.7, 9% (2.8)	71.4 (2.3)	1.10	0.003	6.7
PtCoFer (used powder)	782.2 (3.9)	71.4 (2.0)	1.05	0.0019	6.6
PtCoFer-M (calcined)	782.8 (4.5)	73.5 (2.5) 71.4, 30% (1.9)	1.44	0.0056	7.2
PtCoFer-M (used)	782.0 (3.8)	72.2 (3.2)	1.04	0.0060	6.5
(PtCofer + SiO_2)-M (calcined)	782.3 (4.2)	72.2 (2.4)	0.5	0.004	4.4
(PtCofer + SiO_2)-M (used)	783.0 (4.3)	71.8 (2.0)	0.86	0.0024	6.6

[a] The binding energies are referenced to the C 1s peak (284.6 eV).

[b] Bulk atomic ratio.

temperature fluctuations. As a result, adhesion loss is a likely cause for concern [30]. 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 [30]. Since the washcoat weight loss we detected during the catalytic runs was under experimental error (mainly due to the manipulation of the sample), a more severe test was applied which consists of an ultrasound treatment [21]. After the treatment described in Section 2, 26 wt.% of KFerrierite was lost, while only 11 wt.% was lost for the washcoat containing silica as a binder. This binding effect of silica is well known and has been reported mainly in three-way catalysts [30].

4. Discussion

A washcoated monolith catalyst should meet three basic conditions to be used under practical conditions: good bonding between the washcoat and the support, optimal washcoat thickness, and of course, the active phase should maintain its catalytic properties after the powder is washcoated. For our PtCoFer catalysts, which in the powder form are very active and selective for the reduction of NO_x with methane [13–15], we found that it is not trivial to maintain this high activity after the powder is washcoated on a cordierite honeycomb.

The present work was focused on following different routes to obtain a monolith washcoated with a PtCoFer catalyst. The preparation of the finished catalysts always involved dipping the monolith into the slurry, blowing air to remove the excess liquid, drying, and calcination. The last step is very important since calcination bonds the washcoat safely to the monolith walls, and is usually done at temperatures of 823 K or higher. Besides, a binder can be used in order to improve the bonding strength. For the washcoating of powders with small particle diameter, which is the case of zeolites, it has been reported that the use of a binder is not essential [31]. However, in the present work, we found that silica as a binder substantially improves the adherence of the coating when the ultrasound test is used to evaluate it. Moreover, silica also has a beneficial effect on the selectivity for N_2, as discussed below.

In a previous work [15] we concluded that a Pt–Co synergism exists, by which activity and water-resistance are improved if compared with Co monometallic catalysts. But in order to obtain the best results, a close interaction between Co and Pt is needed. Calcination and/or reduction between exchanges leads to preferential platinum expulsion from the zeolite lattice and the consequent drop in selectivity. On the other hand, the most selective catalysts contain Co^{2+} at exchange positions plus small clusters of cobalt and platinum oxides. Thus, it is reasonable to think that all these features must be searched in a washcoated monolith in order to obtain an active, stable behavior. As a matter of fact, the monolithic catalyst obtained from the sequence: CoFer washcoating—calcination at 823 K—Pt exchange—calcination at 623 K—and finally reduction in hydrogen at the same temperature, resulted in a catalyst with poor selectivity (Table 2) because one of the rules mentioned above was broken (calcination between exchanges results in a poor Co–Pt interaction).

One may conclude that the best way to prepare the monolithic catalyst is the coating with PtCoFer, thus eliminating the intermediate calcination step between exchanges. However, after calcination at 823 K and reduction at 623 K, this solid shows poor activity for NO_x abatement (Table 2). We have found the origin of this deactivation phenomenon in the high calcination temperature before reduction, as also observed in the powder catalyst.

Interestingly, when 2% high surface area SiO_2 acting as a binder was added to the PtCoFer suspension, the washcoated catalysts behaved as well as the starting powder (Fig. 2). This improvement in selectivity is also observed for powder samples mixed with silica in a slurry. As said before, both powder and monolithic PtCoFer catalysts calcined at 823 K prior to reduction show null NO_x conversion, while the same sample mixed with SiO_2 in a slurry retains good activity (Table 2). By analyzing the TPR results, we can correlate the activity of the samples for NO_x reduction with the high temperature peak that corresponds to Co^{2+} exchanged species, a fact that has already been reported in the literature [23]. Besides, it is well known that Co_3O_4 is not selective for the reaction under study. Accordingly, it can be seen that the TPR of PtCoFer calcined at 623 K (active sample) both fresh and used presents a well-defined high-temperature peak while

for PtCoFer calcined at 823 K and used (non-active sample) the main peak is at low temperature, which is characteristic of cobalt oxide (Fig. 3B). It should be pointed out that the temperature of the said peak is lower than the reduction temperature of massive Co_3O_4, which can be ascribed either to a catalytic effect of Pt or to the small size of the crystals (or both). Similarly, the washcoated samples that show the lowest temperature peak are non-selective (Fig. 4B). On the other hand, if powder and washcoated samples are compared, in the case of the samples prepared without a binder, some differences are observed as reported in Section 3. In the case of samples washcoated using a binder, except for the difference upon the onset of reduction, both patterns look very much alike (compare Figs. 3 and 4). The TPR profile of the SiO_2 containing monolith is similar to the profile obtained with active PtCoFer powders. This result may indicate that the effect of the binder is to preserve the characteristics of the starting active powder.

The main information obtained from the XPS experiment is that the binding energy of Co $2p_{3/2}$ corresponding to Co^{2+} ions located at exchange positions. There is no evidence of the presence of Co^{2+}/Co^{3+} in the cobalt oxide matrix with this technique. Note, however, that the TPR data is consistent with the presence of cobalt oxide, which goes undetected by XPS.

The XPS data provides another significant clue: the Pt/Si ratio of the washcoated PtCo with a binder is the same as that measured for the powder. However, when a binder was not used, the Pt/Si ratio increased by a factor of three (Table 6). Thus, the segregation of Pt in the sample prepared without SiO_2 could contribute to the poor performance. This is consistent with the high methane conversion observed in the unselective catalyst. The easily accessible Pt crystals, located in the zeolite outer surface burn out the methane leaving the NO_x molecules unreacted. In fact, it is known that Pt is not a good catalyst for the SCR of NO_x when methane is the reductant [13].

This result led us to think about the reason for Pt segregation. The answer is found in the treatment at 823 K which was performed with the aim of improving the adherence or the PtCoFer film. A similar Pt segregation phenomenon was observed for PtInFer catalysts [32]. As a matter of fact, when we treated the PtCoFer powder in O_2 at 823 K (before the reduction at 623 K), an unselective catalyst was obtained (Table 2). Simi-

lar to the PtCoFer monolith, this solid is only active for methane combustion.

The question now is why the silica protects the properties of the PtCoFer during the calcination process. The surface chemistry of CAB-O-SIL fumed silica is important and may be responsible for the phenomenon observed. Due to hydroxyl groups attached to silicon atoms on the particle surface, the fumed silica is capable of hydrogen bonding with zeolite crystals during the slurry process. The small particle diameter of this material (5–30 nm) makes that phenomenon feasible, thus impairing both the Co and Pt coalescence on the zeolite outer surface. However, this is only matter for speculation and further studies are in progress to elucidate this behavior.

5. Conclusions

- PtCoFerrierite washcoated on a ceramic monolith shows a performance similar to that of the powder catalyst when 2 wt.% of CAB-O-SIL is added to the slurry. Other ways of washcoating without a binder were attempted, but all of them resulted in catalysts with poor selectivity for the reduction of NO_x with methane (Figs. 1 and 2, Table 2).

- All the selective solids for N_2 production show Co^{2+} at exchange positions plus highly dispersed Co_xO_y species. The presence of Co_3O_4 leads to unselective catalysts, this oxide being formed in larger proportion when bimetallic catalysts without added silica are calcined at 823 K or higher temperatures. The addition of silica prevents the Co_3O_4 formation.

- Another important difference observed between the chemical properties of the selective washcoated monolith and the ones with low selectivity was the lower Pt/Si surface ratio of the former. As seen by XPS, a Pt/Si ratio of 0.0024 is measured for the catalyst prepared with a silica binder, which is similar to the bulk ratio obtained from chemical analysis (Table 6).

- The Pt excess on the surface of the washcoated monolith prepared without a binder (Pt/Si ratio is ca. 0.006) may contribute to the observed low activity for NO_x reduction. It is well known that isolated Pt is not a good catalyst for the SCR of NO_x with methane, because it favors the deep oxidation

of methane with oxygen. On the other hand, segregated Pt is not in intimate contact with Co sites, which is a necessary factor in these bimetallic catalysts. The addition of the SiO_2 binder impairs the formation of Pt clusters on the surface.

- As in the case of powder PtCo zeolite catalysts, both reduction and calcination treatments are detrimental to the catalytic activity when performed between cationic exchanges. The heat treatments lead to Pt–Co segregation that negatively affects the selective behavior of the bimetallic formulations.

Acknowledgements

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