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Preparation and characterization of Pd–Co/sulfated zirconia catalysts for no selective reduction by methane

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Abstract

Palladium and cobalt bimetallic catalysts supported on sulfated zirconia (PdCo/SZ), obtained from different precursors of Pd (nitrate and acetylacetonate), were prepared to study their influence on the selective reduction of NO by CH_4 (SCR–CH_4). Catalysts with nominal Pd and Co concentrations of 0.2 and 2 wt%, respectively were characterized by XRD, DRS, XPS and Raman microprobe spectroscopy. The Raman signals denote a superficial increase of the zirconia monoclinic phase during the preparation stage in the catalysts obtained from $Pd(NO_3)_2$ but structural alterations in the surface were not observed when the organic palladium salt was used. Co^{2+} presence, very propitious for this reaction, was determined in fresh catalysts. Catalysts used in reaction exhibit the presence of Co_3O_4 and PdO agglomerates on the surface, loss of sulfates and a total transformation of the tetragonal to monoclinic phase on the support surface. Influence on SCR–CH_4 of the Pd catalytic precursor was not detected.

The catalyst from $Pd(NO_3)_2$ showed better stability than the catalyst from $Pd(CH_3COCH{=}C(O{-})CH_3)_2$ precursor.

1. Introduction

The selective catalytic reduction of NO by hydrocarbons in oxidizing atmosphere (SCR–HC) was proposed in 1990 as an alternative to the ammonia as reductant for the elimination of nitrogen oxides from combustion exhaust. Iwamoto [1] and Held et al. [2] demonstrated that alkanes and alkenes reduce the nitrogen oxides in presence of zeolitic catalysts exchanged with transition metals. Different authors have reported that zeolitic catalysts of noble metals and/or cobalt are very efficient for the NO_x reduction by methane [3–5]. However, the low catalytic stability of these preparations has led to the search of materials with higher tolerance to deactivation and highly selective in the presence of excess oxygen for the reaction, thus proposing the use of acid oxide supports [5,6] or the combinations of different active metals [7,8]. The conjunction of Pd with low cost metals is a good possibility for this reaction. Among supports, the sulfated zirconia is comparable to zeolites MFI type, providing similar acidity but better hydrothermal stability.

Consequently, Pd and Co supported on sulfated zirconia represent an interesting alternative for SCR–HC catalysts, since they have the advantage of being more resistant to water vapor and to SO_2, both components present in combustion exhaust where these materials have to operate. Previous works have demonstrated that the cooperation of several species favors strongly the NO reduction [9,10]. The type of metallic precursor used, which plays an important role in active species formed, favors this cooperation. In our case, the interest is focused in the determination of the kind of active species (Pd, Co) produced during the

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preparation stage of the catalysts as well as their modification and the structural changes of the support during reaction. In addition, it is important to determine these active species especially in presence of water vapor and high temperatures, proper conditions of SCR–HC. In order to analyze the effect of precursors on the catalyst performance, to elucidate the nature of the active sites and the factors that affect their formation on the catalyst, different characterization techniques were used such as XRD, DRS, XPS and Raman microspore spectroscopy.

2. Experimental

2.1. Catalyst preparation

Series of bimetallic catalysts containing Pd and Co were prepared by incipient wetness impregnation on sulfated zirconia (Mel Chemical Co., $S_g = 467\ m^2\ g^{-1}$, $V = 0.21\ cm^3\ g^{-1}$), previously calcined at 823 K. The Pd load of these catalysts was performed by using solutions of two different salts. These solutions were prepared in water for $Pd(NO_3)_2{\cdot}xH_2O$ (Aldrich) and in toluene (Merck) for $Pd(CH_3COCH{=}C(O{-})CH_3)_2$ (Aldrich). For the bimetallic catalysts, an aqueous solution of $Co(CH_3COO)_2 \cdot 4H_2O$ (Riedel-deHaën) was used in all cases. Co was also incorporated in second term by incipient wetness impregnation. Materials containing 0.2 wt% of Pd and 2.0 wt% of Co were obtained. These were named CoPd(acac)/ZS and $CoPd(NO_3)$/ZS, where the first metal in the denomination corresponds to the last metal loaded in the procedure. Pd precursor salts are indicated between parentheses.

Once Pd was incorporated to the support, it was dried at 383–393 K for 12 h and calcined up to 723 K at a heating rate of 2 K min^{-1} in a pure oxygen flow of 10 cm^3/min. The Co was incorporated secondly by using the same procedure.

2.2. Catalyst characterization

After calcination, samples were characterized by Raman microprobe, XPS, UV–vis DRS and XRD.

Textural parameters, specific surface and pore volume, were determined by nitrogen adsorption at 77 K, in an Accusorb 2100E Micrometrics equipment. Data were interpreted using the BET equation.

The S content in fresh and used samples was determined by TGA in a Shimadzu 50 analyzer over 0.015 g sample heated at a rate of 10 K min^{-1} in 20 $cm^3\ min^{-1}$ air stream.

Raman spectra were obtained in a Lab RAM Infinity (Jobin Yvon) spectrometer equipped with a liquid nitrogen detector with spectral resolution of 3 cm^{-1}. The spectrometer was calibrated using the Si line at 521 cm^{-1} MoO_3 lines at 818 and 996 cm^{-1}. The support was taken as reference.

XPS spectra were recorded on a Leybold-Heracus LHS 10 spectrometer in FAT mode (50 eV) using Al Kα radiation. The pressure inside the analysis chamber was lower than 10^{-9} Torr. The following regions were acquired by a computer in a sequential manner: Co2p, O1s, C1s, Zr3d, S2p. BE were referenced to the Zr3d5/2 peak at 182.5 eV. Data analysis involved smoothing non-linear Shirley-type background subtraction and curve fitting using mixed Gaussian–Lorentzian function. Intensity ratios were obtained from the area of the peaks and were used to determine the surface composition, using sensitivity factor methods.

The morphology of catalysts was examined by Philips SEM 505 equipment. A DXPRIME 10 equipment connected to the microscope was used to analyze the chemical composition and estimate the Co and Pd distribution in the catalysts by EDX.

X-ray diffraction diagrams were obtained in a Philips PW 1732/10 equipment using Cu Kα radiation.

The characterization of Co species was carried out in a Varian UV–vis DRS equipment in the wave length range between 200 and 800 nm.

2.3. Catalytic activity

The NO selective reduction with methane was carried out in a continuous flow system with a fixed bed reactor at atmospheric pressure. The temperature was varied between 473 and 873 K and a GHSV of 30,000 h^{-1} (0.4 g of catalysts, 90 $cm^3\ min^{-1}$ flow rate). The reactor was fed with a mixture containing 2000 ppm of CH_4, 500 ppm of NO, 2% of O_2, 6% of H_2O and He as balance. The water was incorporated to the reaction stream through a saturator at 333 K. Previously, the catalyst was activated in the reaction mixture at 973 K with a heating rate of 2 K min^{-1}. The feed and the effluent of the reactor were analyzed by a Shimadzu GC-8A on-line chromatograph, using a CTR1 (Altech) column, thermal conductivity detector and He as carrier gas.

Catalyst stabilities were determined at the maximum conversion temperature for 50 h in 6% water vapor presence in the feed. The reaction conversion was calculated according to:

$$X_{NO} = (2N_2/NO^0)100$$

$$X_{CH_4} = 100(CH_4^0 - CH_4)/CH_4^0$$

where (0) indicates initial condition.

3. Results and discussion

3.1. Textural properties

In order to analyze the temperature effect over textural properties, the specific surface and the pore volume of the calcined support and catalysts were determined. Table 1 shows the specific surface, pore volume and S content for sulfated zirconia and the catalysts calcined at 823 and 963 K, these temperatures correspond to the maximum temperature at which samples were calcined and exposed during the reaction test.

Table 1
Textural properties of fresh and used materials

Muestra	S_{BET} (m^2/g)	V_p (cm^3/g)	S content (%)
Commercial sulfated zirconia (MEL)	467	0.21	8.6
Sulfated zirconia, calcined at 823 K	162	0.20	8.8
Sulfated zirconia, calcined at 963 K	97	0.15	–
CoPd/SZ fresh, support calcined at 823 K	140	0.14	8.5
CoPd/SZ used, support calcined at 823 K	58	0.09	5.8
CoPd/SZ fresh, support calcined at 963 K	83	0.14	–
CoPd/SZ used, support calcined at 963 K	56	0.12	–

The support calcination produces an important loss of the specific surface that increases with the temperature increase. In fresh catalysts, a decrease of textural parameters is observed, which can be attributed to the impregnation step. The used catalysts have shown an important loss of specific surface area during the reaction, even for the catalyst in which sulfated zirconia calcined at 963 K was used. The variation in the measured surface area could be attributed to the elimination of sulfates and the change in crystalline phase from the zirconia, according with the S% content determined by TGA and the spectroscopic analysis, respectively. The pore volume was also affected during the preparation and reaction steps.

3.2. Raman microprobe, XPS and DRS spectroscopy

The Raman spectrum of the sulfated zirconia calcined at 823 K used as support shows the lines at 148 and 263 cm^{-1} assignable to tetragonal phase and the lines at 170 and 190 cm^{-1} to monoclinic phase. In the 800–1500 cm^{-1} spectral region, lines of the sulfate species are visible.

The catalyst obtained from Pd acetylacetonate does not show marked structural changes with the support, while the catalyst obtained from Pd nitrate shows an increase and predominance of the zirconia monoclinic structure [11].

The catalyst extracted from the reactor, obtained from Pd acetylacetonate precursor, shows a higher proportion of monoclinic phase in the zirconia and a strong attenuation of sulfate signals when it is compared with the fresh catalyst (Fig. 1).

Fig. 2 shows the Raman spectra of fresh (a) and used $CoPd(NO_3)/SZ$ catalyst, with (c) and without water vapor (b). The spectrum of catalyst used in wet feed shows a line at 649 cm^{-1} attributed to the formation of agglomerated PdO [12] and Co_3O_4 phase (519, 614 and 686 cm^{-1}) [13] and to an attenuation of the signal corresponding to sulfate species.

XPS spectra of Co–$Pd(NO_3)/ZS$ catalysts, fresh and after reaction were analyzed. For the fresh catalyst, the $Co2p_{3/2}$ signal at 781.5 eV, indicate the presence of Co(II) species [14]. In the used sample, coexistence of Co(II) and Co(III) species is observed. Table 2 shows the surface composition for the two samples. These results suggest that the catalytic performance resulted in a loss of sulfur species, whereas the cobalt dispersion was practically unaffected.

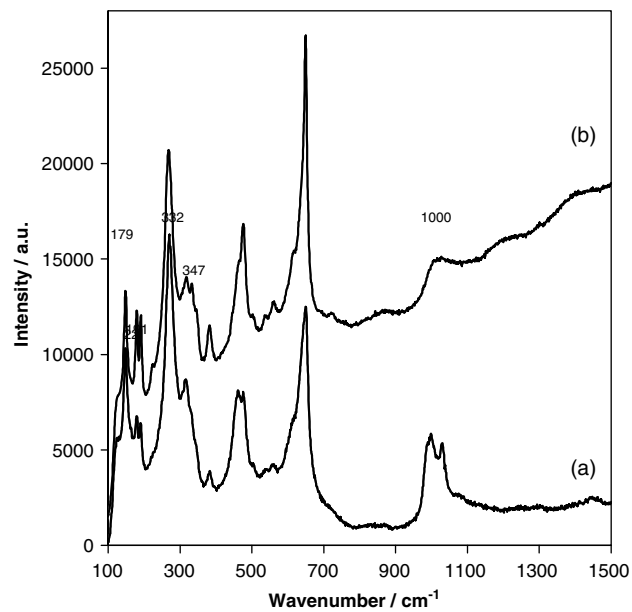

Fig. 1. Raman Micropore patterns of CoPd(acac) catalyst. (a) Fresh sample, (b) sample extracted from the reactor.

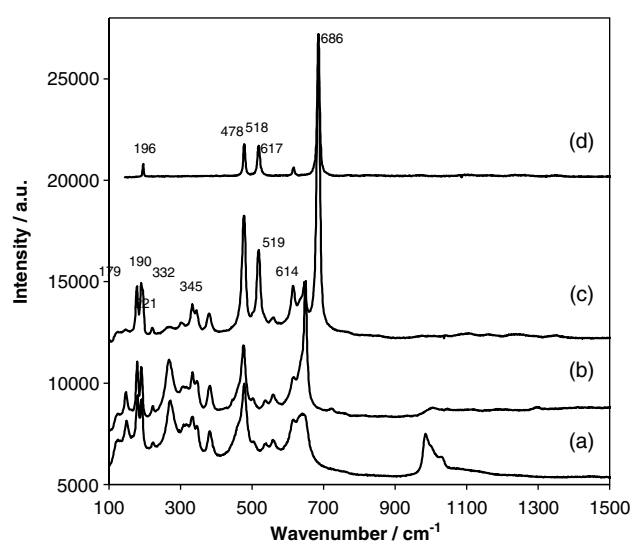

Fig. 2. Raman micropore patterns of $CoPd(NO_3)/ZS$ catalyst. (a) Fresh sample, (b) after reaction without water vapor in the feed, (c) after reaction with water vapor, (d) Co_3O_4.

Fig. 3 shows the UV–VIS–NIR spectra for $CoPd(NO_3)/SZ$ catalyst. Samples treated with water show a band between 700 and 800 nm corresponding to segregated

Table 2
Surface composition of Co–Pd(NO_3)/SZ catalysts[a]

Sample	nCo_{2p}/nZr_{3d}	nCo_{2p}/nS_{2p}	nS_{2p}/nZr_{3d}
Fresh catalyst	0.042	0.36	0.11
Used catalyst	0.051	0.65	0.09

[a] Surface atomic ratio.

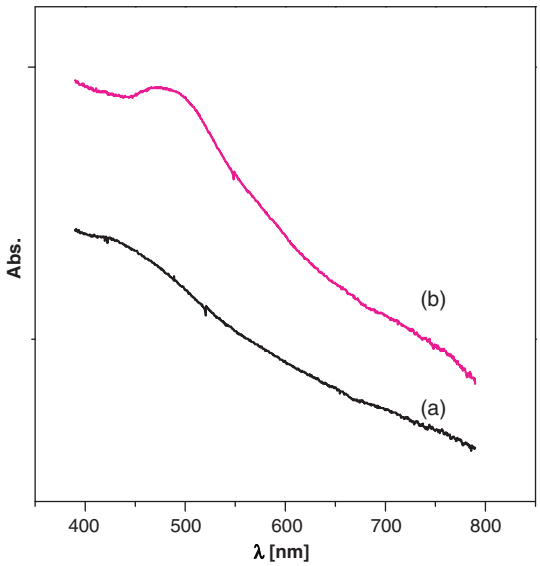

Fig. 3. Diffuse reflectance spectra of CoPd(NO_3)/ZS catalyst. (a) Fresh sample, (b) used catalyst.

Co(III) species from Co_3O_4 [15]. An important increase in the signal at 480–500 nm was observed corresponding to Co^{2+} electronic transition in an octahedral environment [16]. These results are in accordance with Raman and XPS data.

XRD spectra (not shown) indicate the presence of tetragonal and monoclinic zirconia for the fresh catalysts, whereas, in the samples extracted from the reactor an increase of the monoclinic phase is observed in agreement with Raman data.

Other crystalline phase was not observed which can be attributed to low metal (Pd, Co) concentrations or a high dispersion on the support surface.

3.3. Catalytic activity

Fig. 4 shows the NO reduction to N_2 and the CH_4 combustion conversions as function of the reaction temperature for both Pd precursors.

Both catalysts presented practical conversion values of NO to N_2 (about 40%) and a weak stability decline for 50 h in the reaction medium at 500 °C and GHSV of 30,000 h^{-1}.

The influence of the catalytic precursor on the initial activity was not observed. This fact is in agreement with XPS results that did not detect differences for the active (Co^{2+}) phase in both samples. However, in stability tests

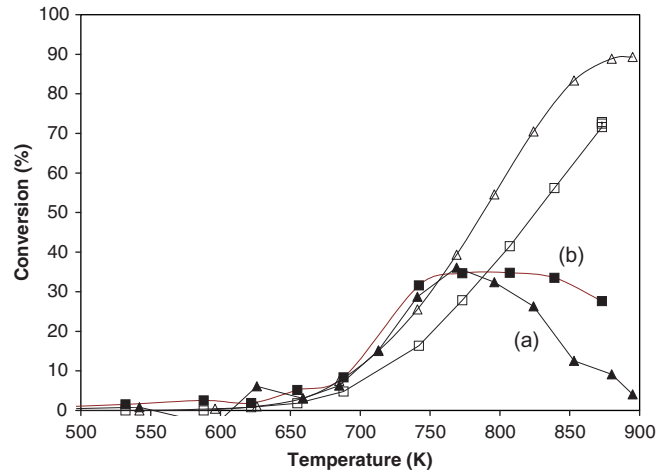

Fig. 4. NO conversion to N_2 (black symbols) and methane combustion. (a) CoPd(NO_3)/ZS, (b) CoPd(ac.ac)/ZS.

during 50 h, the catalysts obtained from $Pd(NO_3)_2$ were more stable than the one obtained from $Pd(CH_3COCH{=}C(O{-})CH_3)_2$. This behavior could be attributed to sulfated zirconia structural modifications and to the sulfate loss during the test in prolonged periods of time.

These catalysts present NO conversion comparable to the one obtained for zeolitic SCR catalysts. On a series of Co/MFI catalysts, Wang et al. reached conversions between 9 and 28% at 500 °C and GHSV = 30,000 h^{-1} with dry feed, while the water vapor addition had a strong suppressing effect on NO reduction with methane [17].

The performance of our catayst is difficult to be compared with the one of the Co–Pd-ZSM5 catalyst reported in the literature [18] due to the fact that operation conditions are very different. However, it is possible to determine that our system presents higher stability with the time on stream than in the case of the zeolitic catalyst. This is an important factor for technological applications.

The 6% water vapor addition to the feed produced a decrease of NO conversion especially at temperatures lower than 773 K and a shift of the temperature window toward higher values, as it is shown in Fig. 5.

The loss in activity could be associated with the formation of PdO aggregates and Co_3O_4 spinel, both of them responsible for increasing the selectivity toward methane combustion.

On the other hand, the support acid sites play an important role in this reaction.

Consequently, structural changes of the support and the elimination of surface sulfate species could be responsible for the deactivation in presence of water vapor in the reaction medium. The change of zirconia phase modifies the acid properties of the support involving specific surface loss of the material [19,20]. Since the selectivity toward NO was ascribed to stabilization of isolated Pd^{2+} on acid sites, the loss of $SO_4^{=}$ may destabilize the Pd^{2+} ions into agglomerated PdO with loss in activity [21,22].

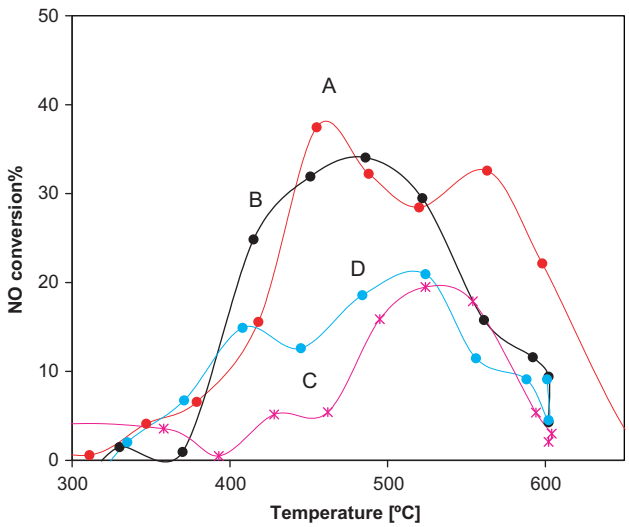

Fig. 5. Influence of vapor water on the NO conversion. (a) $Pd(NO_3)Co/SZ$ catalyst activated at 700 °C, (b) reaction without water in the feed, (c) feed with 6% vapor water, (d) reaction after water remotion.

After water vapor removal from the feed, the catalyst recovers partially its activity. These results would indicate a partial inhibition of the adsorption of reagents by water presence, and also a catalyst deactivation by modification of the active phase as it was determined by Raman spectroscopy.

4. Conclusions

Impregnation of sulfated zirconia with Co and Pd led to a series of catalysts, with good activity and stability for technological applications in the SCR–NO by methane. The best catalyst was that one obtained by inorganic Pd precursor, where the cobalt is present as Co(II) species occupying octahedral sites on monoclinic sulfated zirconia.

The presence of water in the reaction media induces modification of structure of active phases showing the formation of PdO and Co_3O_4 aggregates. The presence of these species is not favorable for the selectivity toward the NO reduction reaction.

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References

[1] M. Iwamoto, in: Proceeding of Meeting of Catalytic Technology for Removal of Nitrogen Monoxide, Tokyo, Japan, 1990, p. 17.
[2] W. Held, A. Koenig, T. Richter, L. Puppe, SAE Paper 900496.
[3] L. Gutierrez, A. Boix, J.O. Petunchi, J. Catal. 179 (1998) 179.
[4] F. Bustamante, F. Córdoba, M. Yates, C. Montes, Appl. Catal. A 234 (2002) 127.
[5] N. Li, A. Wang, Z. Liu, X. Wang, M. Zheng, Y. Huang, T. Zhang, Appl. Catal. B 62 (2006) 292.
[6] F. Figueras, J.L. Flores, G. Delahay, A. Giroir-Fendler, A. Bourane, J.-M Clacens, A. Desmartin-Chomel, C. Lahaut-Burnouf, J. Catal. 232 (2005) 27.
[7] Z. Liu, J. Hao, L. Fu, T. Zhu, J. Li, X. Cui, Appl. Catal. B 48 (2004) 37.
[8] L. Gutierrez, E. Lombardo, J. Petunchi, Appl. Catal. A 194–195 (2000) 169.
[9] C.E. Quincoces, S. Guerrero, P. Araya, M.G. González, Catal. Commún. 6 (2005) 75.
[10] C.E. Quincoces, M. Incollá, A. De Ambrosio, M.G. González, State Surf. Sci. Catal. 143 (2002) 925.
[11] K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, second ed., Wiley Interscience, NY, 1970.
[12] K. Otto, C.P. Hubbard, W.H. Weber, G.W. Graham, Appl. Catal. B 1 (1992) 317.
[13] B.J. Adelman, W.M.H. Sachtler, Appl. Catal. B 14 (1997) 1.
[14] J. Lojewska, W. Makowski, T. Tyszewski, R. Dziembaj, Catal. Today 69 (2001) 409.
[15] I.D. Lick, A. Carrascul, M.I. Ponzi, E.N. Ponzi, I.L. Botto, Mater. Chem. Phys. 92 (2005) 327.
[16] C. Cabello, I. Botto, F. Cabrerizo, M.G. González, J.H. Thomas, Adsorpt. Sci. Technol. 18 (2000) 591.
[17] X. Wang, H. Chen, W.M.H. Sachtler, Appl. Catal. B 29 (2001) 47.
[18] J.A.Z. Pieterse, R.W. van den Brink, S. Booneveld, F.A. de Bruijn, Appl. Catal. B 39 (2002) 167.
[19] T. Yamaguchi, Catal. Today 20 (1994) 199.
[20] B. Xu, W.M.H. Sachtler, J. Catal. 167 (1997) 224.
[21] A. Ali, W. Alvarez, C.J. Loughran, D.E. Resasco, Appl. Catal. B 14 (1997) 1.
[22] Y.-H. Chin, W. Alvarez, D. Resasco, Catal. Today 62 (2000) 159.