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Pillared clay and zirconia-based monolithic catalysts for selective catalytic reduction of nitric oxide by methane

A. Bahamonde*, F. Mohino, M. Rebollar, M. Yates, P. Avila, S. Mendioroz

Instituto de Catálisis y Petroleoquímica, CSIC, Camino de Valdelatas S/N, Campus UAM, 28049 Madrid, Spain

Abstract

New monolithic catalysts based on zirconia and pillared clays (PILC) have been studied for NO_x removal by CH_4 in the presence of oxygen. A comparative study of the influence of ZrO_2 from various commercial sources for the system Pd–ZrO_2 and the effect of the noble metal chosen for the system NM–PILC was carried out, trying to correlate the catalytic activity with the physico-chemical properties of these catalysts. The obtained results indicate that structure and surface acidity of the support plays an important role on the selectivity to NO_x reduction, although properties such as the surface area or pore volume could also determine the overall activity of the monolithic catalysts. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Monolithic catalysts; Pillared clays; Zirconia; Nitric oxide; Methane

1. Introduction

Nitric oxide emissions from combustion facilities is one of the main pollutants that contribute to the formation of acid-rain, smog and ground level ozone. Therefore, strict legislation [1–3] around the world has led to develop efficient $DeNO_x$ technologies in order to preserve the global environment.

Selective catalytic reduction with ammonia is one of the most extended and efficient commercial $DeNO_x$ processes for nitric oxide removal from stationary sources. However, there are some undesirable features with the use of NH_3 as a reductant, such as the concern over ammonia slip. In this respect, SCR of NO_x with hydrocarbons in the presence of oxygen has attracted much attention since Held et al. [4], Hamada et al. [5] and Iwamoto et al. [6] reported the catalytic activity of different zeolites. Following the patent literature [7,8], a number of catalysts, most of them based on ion-exchanged zeolites or metal oxides, have been developed with varying success, using hydrocarbons as reductants.

The use of methane as a selective reductant is highly desirable and perhaps an alternative approach for NO_x emissions control for both mobile and stationary sources because natural gas (mainly CH_4) is readily available and abundant around the world, and widely used as a fuel in many industrial facilities. However, little progress had been made until recently when Li and Armor [9,10] announced that selected metal exchanged zeolites (Co-ZSM-5) were effective catalysts for the novel SCR of NO_x by CH_4 in the presence of excess oxygen.

The use of zeolite-based catalysts for this $DeNO_x$ process present important drawbacks due to their low thermal stability and severe deactivation by the presence of water or SO_2 in the inlet gases, whereas metal oxide based catalysts usually have a narrow operative temperature window in the standard lean-burn operating conditions.

Pillared interlayer clays (PILCs) have been used in a wide range of reactions including SCR of NO with NH_3 [11]. These catalysts offer considerable Brönsted

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* Corresponding author. Fax: +34-915854760.
E-mail address: abahamonde@icp.csic.es (A. Bahamonde).

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acidity, like zeolites, in addition to residual exchange cations which can be exchanged by metal cations from the active phases. PILCs present a tailored pore structure, perfectly tunable by exchange, which can lead to better active phase and reactant diffusion, and finally, depending on pillaring agent, to improve water vapor and SO_2 resistance. Noble metals on solid acids [12] have shown much higher NO_x reduction rates than mixed oxides or perovskites alone [13].

Therefore, the aim of this work has consisted in developing active catalysts for NO_x removal by CH_4 in the presence of oxygen. Pillared clays (PILC) and zirconia conformed by a new manufacturing procedure to monolithic shape have been used as supports for noble metal based catalysts for this process. In this paper we present the preliminary results.

2. Experimental

Two series of catalysts, Zr and PILC, were prepared on home-made honeycomb supports, manufactured by extrusion of different ceramic pastes to produce square-cell monoliths with a pitch of 3.54 mm, 0.90 mm wall thickness and a cell density of 8.9 cell cm^{-2}.

Zr series catalysts were prepared on zirconia-based monolithic supports. The monoliths were manufactured from a mixture of zirconia (from different commercial sources, Table 1), and sepiolite (supplied by Tolsa, S_{BET}: 100 $m^2\,g^{-1}$ after heating at 650°C), used as permanent inorganic binder in a 50 wt.% proportion. Water was added to the powder mixture, that was then kneaded and extruded in monolithic shape. Subsequently, the green bodies were dried and heat treated at 650°C for 4 h in an air atmosphere. 0.6 wt.% Pd was incorporated on the zirconia-based monoliths by incipient wetness impregnation from an aqueous acid solution of anhydrous palladium chloride (Riedel-da Haën), and afterwards heating at 650°C for 4 h in an air atmosphere. The obtained catalysts are denominated as Pd–Zr1 (zirconia from MEI), Pd–Zr2 (zirconia from Millenium) and Pd–Zr3 (zirconia from SEPR), respectively.

PILC series was based on 'pillared' materials. Bentonite from Cabañas (Toledo, Spain), supplied by Tolsa (98% montmorillonite, S_{BET}: 132 $m^2\,g^{-1}$, total pore volume: 0.848 $cm^3\,g^{-1}$ and 74 meq/g clay CEC), was used as the starting material. Al–PILC was prepared, following the method described by Storaro et al. [14], from a 50/50 w/w clay suspension in acetone and a 50 wt.% aqueous solution of Locron (a form of Al Keggin cation) at a 20 meq/g clay ratio used as pillaring agent. The clay suspension was stirred for 24 h, then the pillaring solution was added dropwise and the suspension was thoroughly stirred for a further 24 h at room temperature, dialyzed with distilled water until chloride free, dried at 60°C and heat treated at 500°C for 2 h. These powdered materials (Al–PILC), mixed with bentonite, as a binder, and water at a 55/15/30 wt.%, were kneaded to get an optimal ceramic paste with adequate rheological properties to obtain good green bodies. The extruded monoliths were carefully dried at room temperature and finally calcined for 2 h at 500°C. Incipient wetness impregnation was used to incorporate 0.6 wt.% Rh, Pd or Pt to the supports from the corresponding precursor salts, $RhCl_3 \cdot 3.7H_2O$, $Pd(NH_3)_4Cl_2$ and $Pt(NH_3)_4Cl_2$, respectively. Finally, the impregnated Al–PILC based monoliths were calcined at 500°C in an air atmosphere for 2 h. Catalysts from PILC series are identified as Pd–PILC, Pt–PILC and Rh–PILC, respectively, in the paper.

Textural and morphological properties were analyzed by nitrogen adsorption and MIP. Surface areas, micro and mesoporosities were calculated from N_2 adsorption–desorption isotherms obtained with a Micromeritics ASAP 2310 equipment. Macroporosity was evaluated from mercury intrusion porosimetry (MIP) using CE Instrument Pascal 140/240. The

Table 1
Source and properties of zirconia raw materials

Commercial name	Source	Purity (wt.%)	SO_3 (wt.%)	Particle size (μm)	BET area (m^2/g)
Zirconium hydroxide XZO682/01	MelChemicals MEI	>94.3	5–6	15	90–100
Zirconium oxide "O" grade	Millenium	>99.75	–	5–9	7–12
ZR 100 S	SEPR	>99.6	–	4–10.4	109

crystalline structure of the phases present in the catalysts were determined by means of X-ray diffraction (XRD) in a Philips PW1710 powder diffractometer over the 5–75° (2θ) region using Cu Kα radiation($\lambda = 0.15418$ nm). Thermal analysis (TA) was carried out on a Netzsch STA409EP in an air flow of 75 ml min^{-1} at a heating rate of 5 min^{-1}. Acidity was evaluated through room temperature ammonia adsorption on samples previously dried at 400°C, 3 h in a PE TGS II thermogravimetric analyzer.

Catalytic activity tests were carried out in an integral monolithic reactor. The influence of reaction temperature (300–500°C) on methane and nitric oxide molar conversions were analyzed. The feed gas composition was: [NO] = 500 ppm, [CH_4] = 5000 ppm, [O_2] = 1.2% v/v and N_2 as balance, and operating conditions: GHSV = 4000 $\text{h}^{-1}$and linear velocity = 0.4 Nm s^{-1} with a total flow of 3600 Nml min^{-1}. Inlet and outlet nitrogen oxides, methane and CO_2 contents were analyzed using a chemiluminiscence NO/NO_x analyzer (SIGNAL 4000 VM), a FID analyzer (HORIBA FIA-510) and a non-dispersive infrared analyzer (HORIBA VIA-510), respectively.

3. Results and discussion

Textural properties of the two series are given in Table 2. Pore size distribution in Zr series (Fig. 1) varies depending on raw material source and particle size. Thus, Pd–Zr1 and Pd–Zr2 catalysts show bimodal distributions with pore sizes around 3000 and 20 nm, and 135 and 50 nm, respectively, while

Table 2
Physico-chemical properties of catalysts

Catalyst	Zirconia source	Acidity (mmol NH_3/g_{cat})	S_{BET} ($m^2\,g^{-1}$)	Total pore volume ($cm^3\,g^{-1}$)	$V_{macropores}$ ($cm^3\,g^{-1}$)	$V_{mesopores}$ ($cm^3\,g^{-1}$)	$V_{micropores}$ ($cm^3\,g^{-1}$)
Pd–Zr1	MEI	0.72	79	0.673	0.498	0.175	–
Pd–Zr2	Millenium	0.29	58	0.530	0.314	0.216	–
Pd–Zr3	SEPR	0.38	88	0.540	0.243	0.297	–
Pd–PILC	–	1.48	193	0.328	0.215	0.075	0.038
Pt–PILC	–	1.28	206	0.330	0.205	0.085	0.040
Rh–PILC	–	1.42	200	0.331	0.212	0.079	0.040

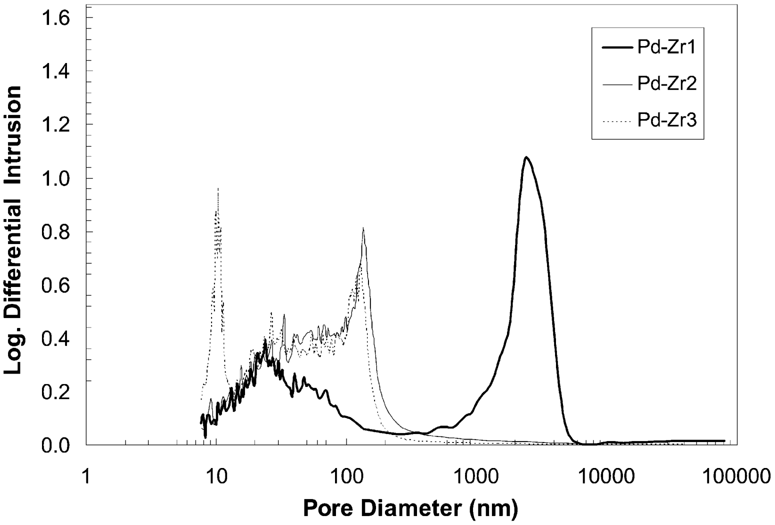

Fig. 1. Pore size distribution of Zr series.

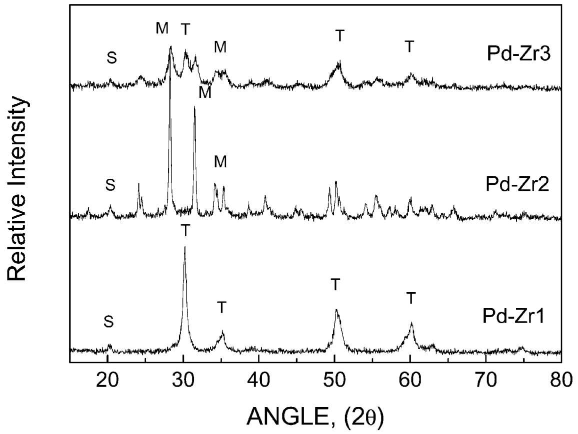

Fig. 2. XRD patterns of Zr series.

Pd–Zr3 monolith presents a trimodal distribution at around 120, 30 and 10 nm.

PILC-based catalysts had similar textural characteristics, as corresponding to the support which was not altered through active phase incorporation. On those samples, microporosity and corresponding S_{BET} are important, and much higher than on Zr series, whereas macro and mesoporosity are smaller.

XRD diffractograms for Zr series are presented in Fig. 2. Where the peaks from sepiolite (S), zirconia-tetragonal (T) or zirconia-monoclinic (M) are indicated. From these patterns some important differences can be seen. Thus, Pd–Zr1 and Pd–Zr2 catalysts show an unique zirconia phase corresponding to tetragonal or monoclinic, respectively, whereas on Pd–Zr3, prepared from zirconia SEPR, a mixture of monoclinic and tetragonal structures was detected. Although the zirconia phase-change from monoclinic to metastable tetragonal is tabulated at 1170°C [15], the presence of sepiolite seems to induce this change at lower temperatures, both phases appearing on Pd–Zr3 after heating at only 650°C.

Surface acidity values, expressed as millimoles of NH_3 chemisorbed per gram of catalyst, are also given in Table 2. Catalyst prepared from zirconia MEI, Pd–Zr1 shows the highest value of this series, as corresponding to its sulfate content. Acidity in PILC series is similar in all samples and is related to the pH of the impregnating solutions (pH Pd sol. = 4.3, pH Pt sol. = 7.0, pH Rh sol. = 1.0) in conjunction with the protonizable OH^- of the support surface.

NO_x and CH_4 molar conversions were determined on all catalysts as a function of the reaction temperature. Moreover, from outlet analysis of NO_2 and CO_2, the percentages of NO transformed in NO_2 and CH_4 in CO_2 were calculated. From these data, the NO_2 formation was studied and the carbon balance for each experiment was closed. In all experiments, the C balances were in the range of $100 \pm 3\%$.

All catalysts offer a similar behavior with the expected typical volcano curve with a maximum for NO molar conversion around 400°C. As an example, the results of Pd–Zr1 are given in Fig. 3.

A comparative study of $DeNO_x$ activity for Zr series is plotted in Fig. 4. The maximum NO reduction was obtained at 400°C, but important differences among NO molar conversions were obtained for each sample. The highest value, close to 20% was obtained with the Pd–Zr1 catalyst, while Pd–Zr2 had almost no conversion in the studied temperature range. The results obtained with the Pd–Zr3 catalyst were intermediate.

Trying to relate these results with the different physico-chemical characteristics of the studied monoliths, it was observed that the best outcomes were obtained with the Pd–Zr1 catalyst with the widest pore diameter (see Fig. 1) and highest surface acidity (see Table 2) of the series; noteworthy, this catalyst showed tetragonal zirconia in its structure. In contrast, the lowest activity was obtained on the Pd–Zr2 with the lowest surface acidity and surface area of all of them, but also with monoclinic structure in the zirconia support. Pd–Zr3 catalysts offers intermediate values in all its characteristics, in activity as well as in acidity and porosity, and its crystalline structure corresponds to a mixture of both phases, monoclinic and tetragonal.

Although it is difficult to distinguish the contribution of each variable in this series, it is important to note that $DeNO_x$ catalytic activity is favored when the zirconia support is in the tetragonal phase. Similar results for zirconia-based catalysts have been reported in the literature for other catalytic processes, and different authors [16–18] have also considered that the presence of a tetragonal phase in the zirconia could be correlated to catalytic activity. Consequently, it is possible that crystallinity could give different results and so lead to different $DeNO_x$ activity, but the surface acidity and even the porous structure of the catalysts could also play an important role in this process.

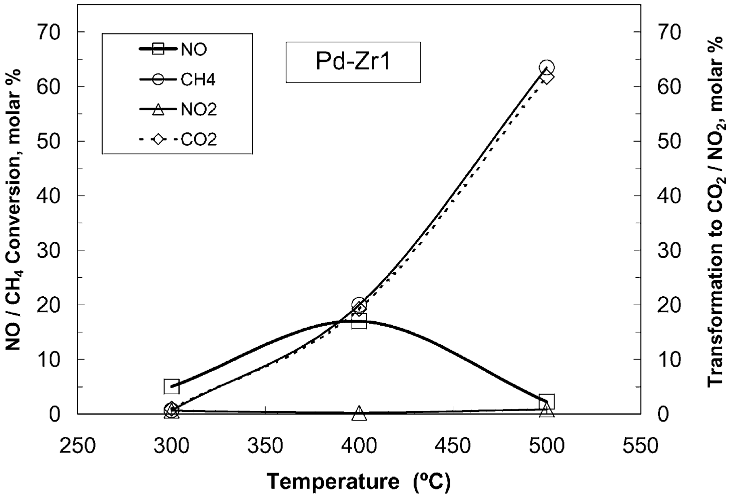

Fig. 3. Influence of reaction temperature on molar NO conversion and formed CO_2 and NO_2 for Pd–Zr1 catalyst. Operating conditions: GHSV = 4000 h^{-1}, linear velocity = 0.46 m s^{-1}, inlet gas composition [NO] = 500 ppm, [CH_4] = 5000 ppm, [O_2] = 1.2 vol.%, and N_2 as balance.

Since the obtained conversion on Pd is far from the values reported in the literature, a change in the active phase was proposed in the series based on PILC as support, and Pt or Rh besides Pd were included. Nitric oxide molar conversions obtained for these catalysts as a function of the temperature are plotted in Fig. 5. Here also, the maximum nitric oxide conversion was observed at around 400°C, and the highest value, around 60% was obtained for the Rh–PILC monolith.

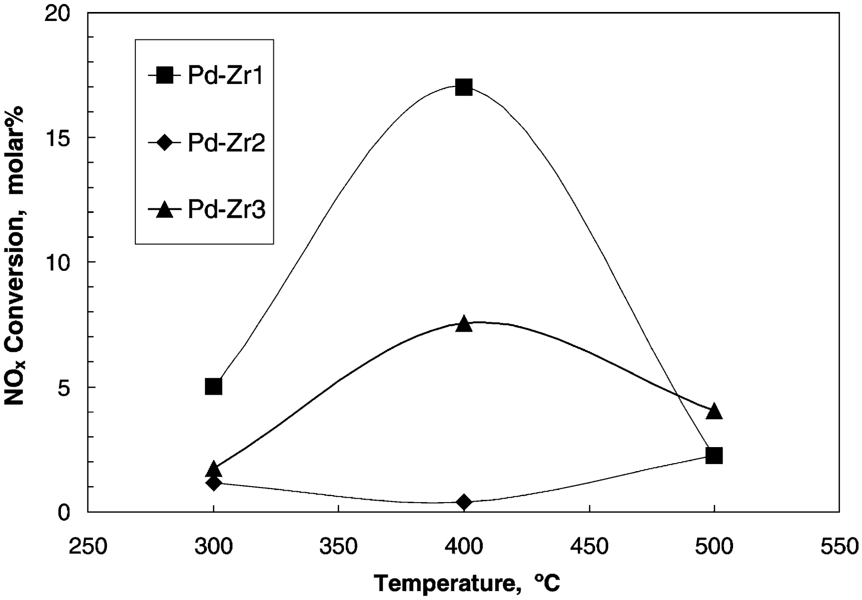

Fig. 4. Influence of operating temperature on NO molar conversion for Zr series. Operating conditions: GHSV = 4000 h^{-1}, linear velocity = 0.46 m s^{-1}, inlet gas composition [NO] = 500 ppm, [CH_4] = 5000 ppm, [O_2] = 1.2 vol.%, and N_2 as balance.

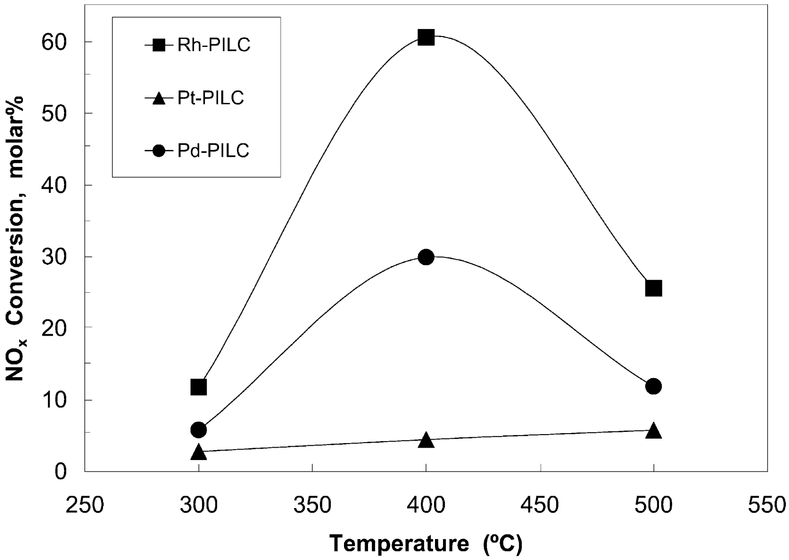

Fig. 5. Influence of operating temperature on NO molar conversion for PILC series. Operating conditions: GHSV $= 4000\,h^{-1}$, linear velocity $= 0.46\,m\,s^{-1}$, inlet gas composition [NO] $= 500$ ppm, [CH_4] $= 5000$ ppm, [O_2] $= 1$ vol.%, and N_2 as balance.

It is important to remark that the NO conversion obtained with Pd–PILC catalyst was higher than that observed with the best catalyst of the Zr series (Pd–Zr1). Considering the differences in the properties of both catalysts (Table 2), this fact seems to indicate that surface acidity can play an important role in NO_x conversion, although factors such as surface area, pore volume or even metal dispersion could also be determinant on the overall activity of the monoliths.

The selectivity of both catalytic series, Zr and PILC series, is compared in Fig. 6 in terms of CH_4 proportions reacting with NO and oxygen. To obtain these values the stoichiometry for NO reduction (Eq. (1)), and CH_4 combustion (Eq. (2)) were considered.

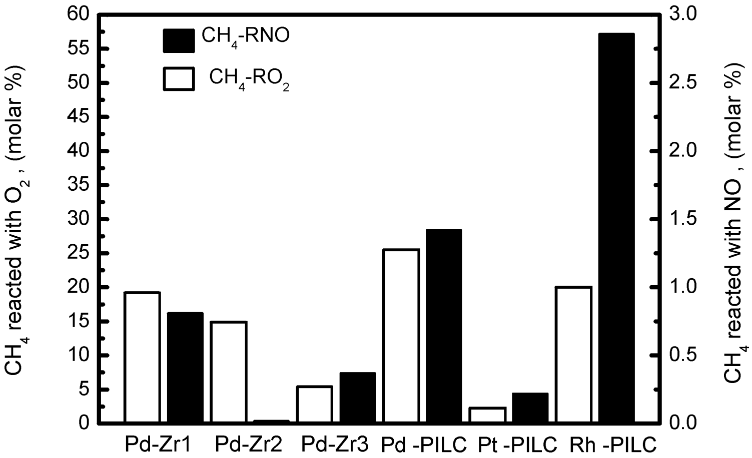

Fig. 6. Comparison of percentage of CH_4 reacted with NO and oxygen for both catalytic series.

$$CH_4 + 2NO + O_2 \rightarrow N_2 + CO_2 + 2H_2O \quad (1)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad (2)$$

These results indicate that when the support is tetragonal zirconia, both reactions, reduction and combustion, take place parallelly, whereas on monoclinic zirconia (Pd–Zr2), mainly CH_4 combustion with oxygen is produced. When PILC catalysts are considered, not only a better activity than on zirconia is obtained in both reactions, but also an improved selectivity to NO reduction against CH_4 combustion is achieved on Rh–PILC, which again could point out to acidity as process determinant. The idea is confirmed by the behavior of Pt–PILC with the lowest DeNO$_x$ activity and surface acidity value of the series. However, more work is in progress to clarify all these results.

4. Conclusions

Monolithic supports based on zirconia and PILC have shown to be very promising in NO$_x$ reduction with CH_4 in oxygen excess, when noble metals are used as catalytic active phases. In general PILC offer a better performance than zirconia, doubling the conversion when Pd is used as an active phase. Rh was found to be more active and selective than Pd and Pt, giving a NO molar conversion of around 60% on Rh–PILC. On zirconia, the catalytic activity to NO total conversion was shown to be dependent not only on the structure of the crystalline phase, but also on its textural and acidic properties. Acidity seems to have an important role in this reaction, the DeNO$_x$ catalytic activity increasing with it in both series.

Acknowledgements

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