Effect of water vapor over Pd–Co/SZ catalyst for the NO selective reduction by methane

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Abstract

The selective catalytic reduction (SCR) of NO by CH_4 in the presence of excess O_2 has been studied on Pd–Co, Pd and Co catalysts supported on sulfated zirconia (SZ) and activated in reaction mixture at 700 °C. After the addition of Co on Pd/SZ, an promoting effect on the catalytic activity was achieved, especially on 0.2%Pd–2%Co/SZ, which showed the maximum NO conversion higher 60% at 500 °C and 31,000 h^{-1}. The bimetallic catalyst presented practical activity in the presence of water vapor. Stable NO_x conversion was obtained for over 50 h in the presence of 6% water vapor. In order to correlate the catalysts composition with their activity, they were characterized by X-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS) and temperature programmed reduction (TPR) techniques.
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Keywords: NO reduction; Methane; Sulfated zirconia; Water tolerance

1. Introduction

The selective reduction of nitrogen oxide with hydrocarbons (HC) is one of the most promising technologies to control NO_x emissions in fixed sources, where it represents an alternative for ammonia used as reducer, as well as in mobile sources that operate with high air/hydrocarbon ratio. Zeolitic catalysts of the Pd/MOR, Pd/ZSM-5, and Co/FER type have been demonstrated to be active for the selective reduction of NO by light hydrocarbons, although they are not stable in the reaction conditions (water vapor, high temperatures, sulfur presence) resulting to be inadequate for practical applications. The activity decrease when water is present in the gas stream, has been attributed to structural modifi-

cations of the zeolitic material as well as to the sintering of the metallic phase. In the Pd zeolite catalysts, Ohtsuka and Tabata [1] have determined that the water vapor promotes the Pd agglomeration, thus deactivating the catalyst. There exists evidence [2] that the activity and the selectivity in the SCR of NO are not only a function of the metallic phase but also of the support acidity. Tests of different acid supports in mechanical mixtures with Pd/SiO_2 [3] demonstrated that sulfated zirconia is one of the most effective materials to promote the Pd activity in the SCR of NO by methane. According to the exposed considerations, the Pd catalyst supported on SZ is presented as an important alternative to replace zeolitic catalysts since it shows comparable catalytic properties and higher stability in sulfur presence, although it does not overcome completely the problem of deactivation by water vapor. Inui et al. [4] reported that a protonated Co-contained silicate was effective for NO reduction with methane in 10% water presence

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in the feed. Since Co/zeolite has also shown to be active for the selective reduction of NO by methane [5] and with the intention of stabilizing the Pd, a multimetallic system based on Co and Pd supported on sulfated zirconia (SZ) was prepared to explore its possibilities in the selective reduction of NO_x by hydrocarbons, containing water vapor in the feed.

In this work, the effect of water vapor on the Pd–Co/SZ system was analyzed and compared with the monometallic systems, Pd/SZ and Co/SZ, for the selective reduction of NO by methane in excess oxygen.

2. Experimental

2.1. Preparation of sulfated zirconia

The sulfated zirconia was prepared by the method known as two steps since in a first stage zirconium hydroxide is prepared, $Zr(OH)_4$, and in a second stage sulfate is used for impregnation, thus obtaining the sulfated zirconium, (SZ). The $Zr(OH)_4$ was prepared from zirconium oxychloride [6]. NH_3 was slowly added (28–30%) to a solution of 100 ml 0.4 M of $ZrOCl_2$, under stirring at 32 °C. Then, the solution was settled at rest for 24 h at room temperature, filtered and washed to remove Cl^- ions. It was left for evaporation at room temperature for 48 h, then, it was dried in a furnace at 100 °C for 2 h. The obtained zirconium hydroxide was sulfated by adding a measured volume of 0.5 M H_2SO_4 solution, so as to reach the equivalent to 5 ml of pure H_2SO_4 per gram of zirconium hydroxide. This process was performed under mechanical stirring ("shaker"), and maintained for 1 h. Afterwards, the solid was separated by filtration and dried for 3 h at 70 °C. Then, it was calcined in air at 550 °C for 3 h.

2.2. Preparation of catalysts

The Pd was added to the prepared support ($Sg = 140$ $m^2\ g^{-1}$, $Vp = 0.21\ cm^3\ g^{-1}$, $rp = 3.3$ nm), using the inorganic salt $(NO_3)_2Pd \cdot 2H_2O$ (Merck) as precursor. For this, an adequate amount of Pd salt was dissolved in 10 cc water, so as to obtain a final metal charge equal to 0.18% wt/wt. This solution was added on the sulfated zirconia by stirring mechanically. The water excess was evaporated maintaining the stirring and was dried at room temperature for 12 h. It was dried at 105 °C, 3 h and calcined in oxygen flow at 500 °C, 1 h.

Co/SZ and Pd–Co/SZ samples were prepared on the SZ and the Pd/SZ calcined at 500 °C, respectively, by impregnation of pore volume at room temperature. An aqueous solution of Co acetate for a suitable metal content (0.5–5 wt%) was used as precursor. Impregnated samples were dried in a furnace and calcined in oxygen at 500 °C for 1 h.

The performance of monometallic and bimetallic solids were tested using various pretreatment procedures prior to reaction. These experiments showed that the samples treated in the reaction mixture at 700 °C after calcination, were the most actives [7]. As a result, all catalysts examined in the current study were pretreated in the reaction mixture at 700 °C prior to any activity testing.

2.3. Characterization of catalysts

Solids prepared were characterized by N_2 adsorption, temperature programmed reduction (TPR), X-ray diffraction (XRD), diffuse reflectance spectroscopy (UV–Vis DRS) and infrared spectroscopy (DRIFT). The catalysts metallic contents were determined by atomic absorption (AA).

The measurements of catalytic activity were performed in a quartz fixed bed reactor containing 0.4 g of catalyst, in a temperature range 200–700 °C and at a space velocity 31,000 h^{-1}. The feed mixture to the reactor was 2000 ppm of methane, 500 ppm of NO, 10% of O_2. The feed and the effluent reactor were analyzed in a "on line" gas chromatograph using a CTR1 column (Altech) at 40 °C, on a thermal conductivity detector and using a He flow of 20 $cm^3\ min^{-1}$ as carrier gas.

The effect of water vapor on the stability of samples was determined by using a feed stream containing 6% water vapor. The scheme of experiments consisted first of measurements of samples in a feed without water, varying the temperature between room temperature and 700° C. Then, the reactor was cooled for 12–15 h, later on, the same sample was measured in feed with water. Finally, it was measured again in a dry feed to observe the activity in water vapor absence.

To compare catalytic activity and selectivity of the mono and bimetallic catalysts the following reactions were considered

$$CH_4 + 4NO \rightarrow 2N_2 + CO_2 + 2H_2O \qquad (1)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (2)$$
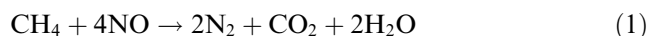
The NO conversions to N_2 were calculated in terms of N_2 production

$$X_{N_2}\% = (2N_2/NO^o)100 \qquad (3)$$

The conversion of methane combustion was calculated as

$$X_{CH_4}\% = \{[CO_2 - N_2/2]/CH_4^o\}100 \qquad (4)$$

The percent selectivities were defined as

$$S(\%) = \{2X_{NO}NO^o/[X_{CH_4}CH_4^o]\}100 \qquad (5)$$

Neither N_2O nor CO were detected.

3. Results and discussion

3.1. Effect of catalyst composition on catalytic activity

In order to study the effect of the metals concentration on the activity, a series of Co/SZ and Pd/SZ samples were prepared containing between 0.5% and 5% of Co and 0.2% and 0.5% of Pd, respectively.

The 0.2% Pd/SZ presented the much higher activity but showed an important deactivation with the temperature and time on line. At temperatures up 500 °C, the SCR activity was not stable even without the addition of water vapor. The Co content slightly affected the SCR–NO in the reaction conditions used in this work. Samples containing Pd and Co charges higher than the mentioned ones, only showed activity for the methane combustion. This behavior can be attributed to an excessive metal charge and to a low metal dispersion on the support.

The NO conversion as a function of the temperature is compared in Fig. 1, on Pd/SZ and Pd–Co/SZ catalysts using a dry feed mixture. The Co addition on Pd/SZ samples increased the NO conversion to N_2 and decreased the maximum conversion temperature indicating a promoter effect of the Co on the NO reduction activity of the catalyst. Under the same conditions at 500 °C the NO conversion increased strongly for the Pd–Co/SZ (64%) with respect to the monometallic Pd catalyst (29%). The bimetallic (Pd–Co/SZ) catalyst showed the advantage of suppressing, partly, the methane combustion (Fig. 1) favoring the selectivity (Eq. (5)) towards the NO reduction. Table 1 shows the catalytic behavior of monometallic and bimetallic samples tested in the NO reduction by methane containing 10% oxygen. These results suggested a cooperative effect of Pd and Co in the selective reduction of NO by methane on bimetallic catalysts.

Table 1
Catalytic activity and selectivity of catalysts[a]

Catalysts [b]	X_{NO} (%)	T_{max} (°C)	X_{CH_4} (%)	Selectivity [c]
Pd/SZ	58	565	98	0.59
Co/SZ	62	524	40	1.55
PdCo/SZ	64	500	52	1.22

[a] Reaction conditions: GHSV: 31,000 h^{-1}, NO: 500 ppm, CH$_4$: 2000 ppm, O$_2$: 10%.
[b] Catalysts pretreated in reaction mixture at 700 °C. Heating rate: 2 °C.
[c] $S = \{2X_{NO}NO^o/[X_{CH_4}CH_4^o]\}$.

3.2. Influence of water vapor on the activity of catalysts

The effect of the addition of 6% vapor water to the feed on the SCR by methane was evaluated on the Pd/SZ, Co/SZ and Pd Co/SZ catalysts. Fig. 2 compares the NO reduction activity of monometallic samples of Pd and Co with the bimetallic catalyst, for equal metal content, at 500 °C. The three catalysts were deactivated in presence of water in the feed, decreasing NO and methane conversions in the temperature range studied. In the Pd–Co/SZ catalyst, the deactivation was reversible and in water absence the NO conversion is completely recovered equal to the case of the Pd/SZ catalyst. This behavior suggests that the water vapor would act on the Pd active sites inhibiting the reactants adsorption, better than modifying them. On the other hand, the Co/SZ catalyst decreased its reduction activity and shifted the operation window to higher temperatures in water presence. This effect was partially reversible when the water was removed without reaching the total recovery of the catalytic activity. This behavior can be associated to the Co_3O_4 formation (observed by DRS) in the Co/SZ catalyst, but it was not detected in the bimetallic catalyst.

In Fig. 3, the variation of both NO and methane conversion with the temperature is presented either in
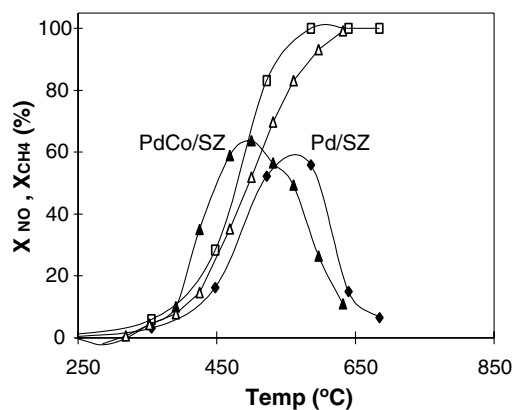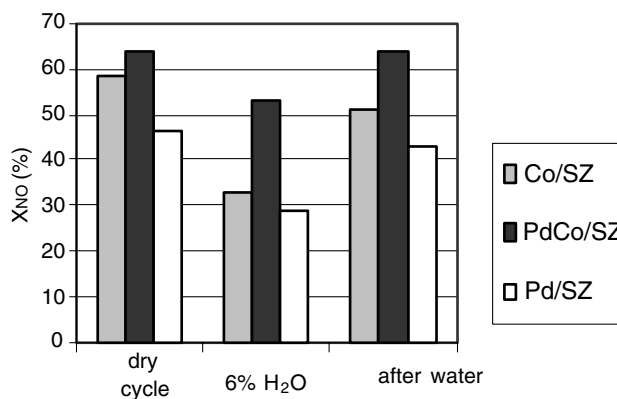

Fig. 1. NO conversion as a function of temperature (black symbols) and methane combustion (open symbols), in Pd/SZ (◆) and PdCo/SZ (▲) samples. Reaction conditions: GHSV: 31,000 h^{-1}, NO: 500 ppm, CH$_4$: 2000 ppm, O$_2$: 10%.

Fig. 2. Effect of water stream over NO conversion for mono and bimetallic catalysts. Reaction conditions: GHSV: 31,000 h^{-1}, NO: 500 ppm, CH$_4$: 2000 ppm. O$_2$: 10%, H$_2$O: 6%, Temp.: 500 °C.
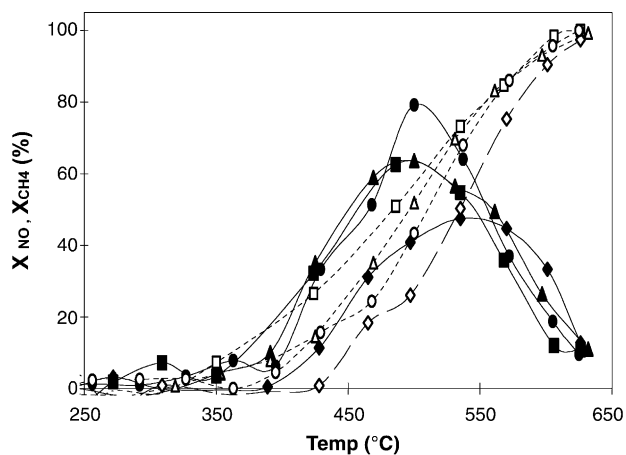
Fig. 3. Effect of water vapor over NO conversion (—) and CH_4 conversion (- - -) as temperature function in PdCo/SZ catalyst, dry feed (curve 1, ▲), 6% water in the feed (curve 2, ◆), first dry cycle (curve 3, ■), second dry cycle (curve 4, ●). Reaction conditions: GHSV: 31,000 h^{-1}, NO: 500 ppm, CH_4: 2000 ppm, O_2: 10%.

Fig. 4. NO conversion on time on stream for mono and bimetallic catalysts at 500 °C. Reaction conditions: GHSV: 31,000 h^{-1}, NO: 500 ppm, CH_4: 2000 ppm. O_2: 10%, H_2O: 6%.

presence or in absence of water in the feed, for the Pd–Co/SZ catalyst. In the presence of water a decrease of NO and of methane conversions, especially at temperatures lower than 500 °C, and a shift of the temperature window towards higher values were observed (curve 2). After removing the water vapor the catalyst recovered its activity (curve 3). An NO activity increase in subsequent experiments to the water treatment was observed in according with a partial inhibition of hydrocarbon combustion (curve 4). This phenomenon could be attributed to an enhancement of catalyst acidity, essential for the generation of highly dispersed species, which were active for NO reduction. This will be subject of future studies to explain such behavior.

3.3. Catalytic stability

One of the most important properties of catalysts, is the stability when operating at long times in the reaction mixture. In order to analyze the behavior of catalysts, the NO reduction activity was determined in presence of 6% water for 50 h at a GHSV of 31,000 h^{-1} and 500 °C. Fig. 4 shows the stability for monometallic and bimetallic catalysts in terms of the NO conversion to N_2 as a function of the time on stream. All samples showed an activity decrease in the first reaction hours, ca. 3 h, before reaching a constant value of NO conversion. At about 30 h, the Pd–Co/SZ catalyst reached a NO conversion stationary value higher than 50% in the presence of water vapor, which was markedly higher than in monometallic catalysts. The methane combustion showed a different behavior, the CO_2 conversion was constant for Co/SZ and Pd–Co/SZ catalysts, while it increased noticeably for Pd/SZ suggesting the PdO formation, highly active for the methane combustion
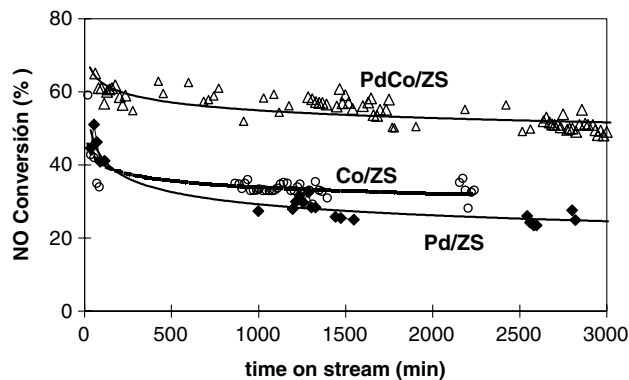
[8]. Adelman and Sachtler [9] state that the PdO formation can be generated by hydrolysis according to the scheme: $Pd^{+2} + H_2O \rightarrow 2H^+ + PdO$. These results suggest that the presence of Co improve the Pd stability perhaps by inhibition of PdO formation.

The initial deactivation in presence of water defined as the NO conversion variation during the 3 first reaction hours with respect to NO conversion at zero time, $d = \Delta X_t/X_i$, was determined for mono and bimetallic catalysts. This deactivation was less pronounced for the bimetallic catalyst ($d = 0.10$) than for the Co/SZ ($d = 0.19$) and Pd/SZ ($d = 0.29$) catalysts. This behavior could be attributed to a synergic effect of both metals on the selective NO reduction by methane. After 50 h when we returned to initial feed (without water), the NO conversion did not change and remained stable for PdCo/SZ sample. However, the Co/ZS and Pd/SZ presented a decrease in the NO conversion.

3.4. Characterization of the catalysts

Fresh samples and those extracted from the reactor were characterized by TPR, XRD and UV–Vis DRS with the aim of correlating the active species and the catalysts performance.

X-ray spectra of the support and Pd–Co/SZ catalysts (not shown), before and after the activation, indicated that during the pre-treatment crystallographic transformations of the support were generated [10]. A transition from the tetragonal ($2\theta = 30.2°$) to monoclinic sulfated zirconia ($2\theta = 28.3°$ and $31.6°$) was observed after catalyst activation in the reaction mixture at 700 °C. The diffractogram of the sample extracted from the reactor was characterized by an increase in the intensity of signals of the tetragonal phase, this indicating a crystallinity increase, and the appearance of some weak signals corresponding to the monoclinic phase. The oxygen presence would be responsible for the change of the crystalline phase under lesser severe conditions than the ones found

usually for the transformation of tetragonal to monoclinic phase [11]. Similar results were observed in Pd and Co monometallic samples. Other crystalline phase was not observed by XRD, which can be attributed to low concentration of metals (Pd, Co) in samples and/ or a high dispersion of these metals on the support surface.

Information about characteristics of the metallic phase was determined by UV–Vis diffuse reflectance spectroscopy and temperature programmed reduction.

DRS spectra (Fig. 5), at wavelengths between 300 and 800 nm, of Pd–Co/SZ catalyst showed the octahedral Co^{2+} presence (550 nm) in the fresh catalyst and tetrahedral Co^{2+} (650 nm) in the sample removed from the reactor (Fig. 3, curve 4) [12]. This change is in accordance with the transformation of tetrahedral to monoclinic phase in the sulphated zirconia observed by XRD spectra, after reaction. The Co/SZ treated with water presented a signal between 700 and 800 nm assigned to Co_3O_4, in agreement with the literature data [13,14], which may be responsible for the loss of SCR–NO selectivity.

TPR patterns of non-calcined catalysts and samples removed from the reactor are shown in Fig. 6. Pd–Co/ SZ fresh samples presented a small peak between 90 and 200 °C that could be attributed to the Pd^{2+} reduction and another two peaks between 400 and 600 °C which would correspond to the reduction of Co_xO_y and sulfate present in the support.

The support (SZ) showed two peaks at 680 and 725 °C assigned to the sulfate reduction. Several researchers [15–17] determined that the sulfated zirconia reduction involves two different processes corresponding to two sulfate species, one species that is reduced to H_2S and another one that is reduced to SO_2. These species were assigned by Dicko et al. [17] to adsorbed and structural sulfate.

Fig. 6. TPR profiles of Co/SZ and Pd–Co/SZ catalysts. Comparison with the sulfated zirconia reducibility.

The catalyst removed from the reactor after reaction showed an asymmetric signal of lower intensity around 500 °C and a small signal in the zone of the lowest temperatures (100 °C). Signals around 500 °C can be assigned to Co^{2+} in agreement with DRS data and TPR signals of the Co/SZ. It is evident that the treatment in the reaction mixture affects the active phase. The Pd presence seems to modify the reducibility of sulfate groups, when comparing support and the bimetallic catalyst reducibility. There are evidence in the bibliography [15] that the presence of Pt facilitates the reduction of S^{6+} to S^{2-} in the sulfated zirconia.

4. Conclusions

Sulfated zirconia loaded with palladium and cobalt exhibited high activity and stability in SCR of NO with methane previous activation in the reaction mixture at 700 °C. The catalytic activity in the bimetallic catalysts would be related to the promotion of Pd/SZ by the presence of isolate Co^{2+} ions. In contrast to known catalysts, Pd–Co catalysts showed higher activity after treatment in water vapor. Stable NO_x conversions higher 50% was obtained for over 50 h in presence of 6% water. By comparing the catalytic performance of Pd and Co monometallic catalysts with that of PdCo/SZ in the presence of water, it was found that the bimetallic catalyst was more tolerant to water and showed better reversibility in activity after removal of water.
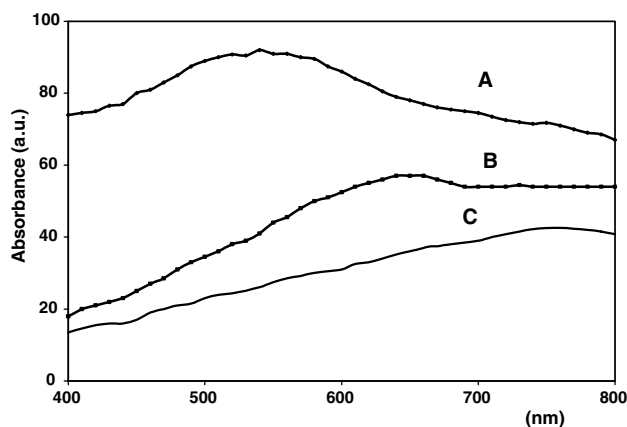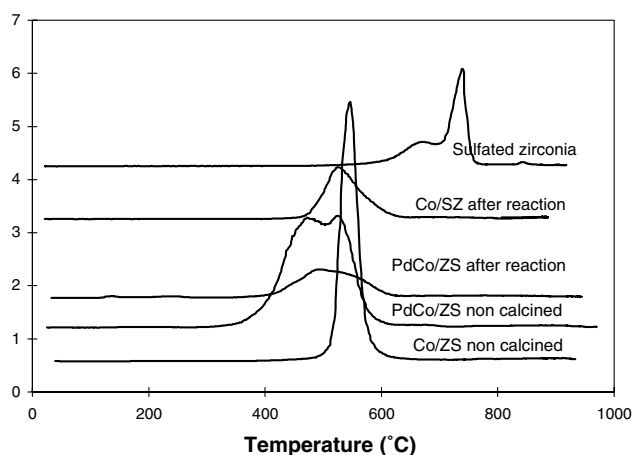
Fig. 5. UV–Vis DRS spectra of Pd–Co/SZr and Co/SZr samples. (A) Pd–Co/SZr calcined, (B) Pd–Co/SZr extracted from reactor, (C) Co/ SZr extracted from reactor.

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