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Influence of oxygen and promoting effect of barium on the reduction of NO_x by ethanol on Pd/ZrO_2 catalyst

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ABSTRACT

The NO reduction by ethanol over barium promoted Pd/ZrO_2 catalyst and the effect of the oxygen on the selectivity were studied. The catalysts were prepared by incipient wetness impregnation with 14.3% of Ba over zirconia and 1% of palladium. The specific surface areas were 58 and 47 m^2/g and the dispersions of Pd were 37% and 30% for the Pd/ZrO_2 and $Pd–Ba/ZrO_2$ catalysts, respectively. The X-ray diffraction patterns indicate the presence of monoclinic zirconia phase on the support and $BaCO_3$, which is decomposed at 715 and 815 °C. Temperature programmed desorption profiles of NO on Pd/ZrO_2 and $Pd–Ba/ZrO_2$ catalyst showed a huge amount N_2 formation for the promoted Ba catalyst. Catalytic results showed high NO conversion even at low temperature, in accordance with the TPD results and an increasing selectivity to N_2 when compared with Pd/ZrO_2. The effect of O_2 in the NO_x reduction with ethanol provoked less NO dissociation and lower selectivity to methane.

1. Introduction

The atmospheric pollution is one of the largest problems in the world causing damages to the environment and human health. The efficiency in combustion and lower fuel consumption has fostered the design of new engines working with higher than stoichiometric air/fuel ratios ($A/F > 14.7$) that is under lean conditions [1]. The resulting excess of oxygen in the gas stream leads to low efficiency of conventional NO_x reduction catalysts and requires efforts to develop an alternative solution. The most promising concept seems to be the use of NO_x storage/reduction (NSR) catalysts for lean conditions. These catalysts, normally containing Al_2O_3 supported noble and alkaline earth metals have been developed and used [2].

The NSR concept is based on the storage of nitrogen oxides by an alkaline or alkaline earth component in the form of nitrates when the engine is operating under lean conditions. Stored nitrates are then selectively reduced to nitrogen during a short fuel rich period [3–6]. Kobayashi et al. [7] observed that the presence of Ba in the Pd catalyst increased the conversion of CO, NO and hydrocarbons due to the formation of nitrite. Besides that, they explain that the addition of Ba, Sr and La affect the electronegativity and basicity of the catalyst, modifying the electronic density of Pd and increasing the activity for NO reduction. Takahashi et al. [3] claim that the electronegativity of the component and the amount of NO_x storage suggests a direct relationship between the basicity and the NO_x storage. Lietti et al. [8] presented a reaction mechanism for the NO_x reduction with Ba species, suggesting the formation of different active components of hydroxide and carbonate. Piacentini et al. [9] observed highly dispersed BaO in the $Pt–Ba/Al_2O_3$ catalyst.

The use of ethanol in gasoline and diesel has been growing [10]. The addition of such compounds reduces the emission of olefins, aromatics and SO_x. However, the use of ethanol, for instance, may increase the direct emission of aldehydes (acetaldehyde and formaldehyde) and also of unburned alcohol [11]. Previously, was reported the reduction of NO_x with ethanol on Pd/ZSM5 catalysts and Pd/ZrO_2 sulfated catalysts. Results showed that ethanol adsorbed form probably ethoxy species that react forming ethylene, besides dehydrogenate forming adsorbed acetate species that react with NO. Excess of O_2 favors ethanol oxidation to CO_2 [12].

The main objective of this work is to study the promoting effect of barium on the Pd/ZrO_2 catalyst for the NO_x reduction with ethanol and the effect of oxygen on the selectivity.

2. Experimental

2.1. Catalyst preparation

Hydrous zirconia was obtained by hydrolysis of zirconium(IV) oxinitrate with a base. Ammonium hydroxide 5 M was used. An aqueous solution of zirconium(IV) oxinitrate was prepared. This solution was added dropwise to an excess of 5 M aqueous ammonia solution (about 150% in excess) with stirring and pH continuously monitored during the entire procedure of precipita-

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tion in the basic range. The samples were dried at 120 °C for 18 h and calcined under flowing air at 500 °C for 1 h.

Thereafter, Ba was impregnated by incipient wetness on ZrO_2 with a 3.1 M barium acetate solution (Aldrich). Finally, 1% of Pd was impregnated by incipient wetness on Ba/ZrO_2 with a $Pd(NH_3)_2(NO_2)_2$ solution (Aldrich). The sample was dried at 120 °C for 18 h and then calcined under flowing air at 500 °C for 1 h and nominated Pd–Ba/ZrO_2 sample. The theoretical barium content was 16%.

2.2. Characterizations

The chemical composition of the catalyst was determined by X-ray fluorescence (XRF) using a spectrometer Rigaku, model Rix 3100.

X-ray powder diffraction (XRD) patterns were recorded in a Rigaku-Miniflex diffractometer using Cu Ka radiation (40 kV to 40 mA) over a 2θ range from 2° to 80°, step size of 0.05° and 2.0 s/step.

BET specific surface area was measured by N_2 adsorption (ASAP 2000-Micromeritics). Before the measurements, the samples were degassed at 300 °C under low pressure.

The H_2 chemisorption measurements were obtained on an ASAP 2000Q (Micromeritics) equipment. Prior to reduction, the catalysts were dried at 150 °C for 30 min. The samples were reduced with pure hydrogen (30 cm^3/min) at 500 °C (5 °C/min). The irreversible adsorption was determined.

The thermogravimetric analyses (TGA) and differential thermal analysis (DTA) (Rigaku TAS-100, with TG 8110) were carried out with sample weight of 14 mg, passing N_2 (53 cm^3/min) and O_2 (4 cm^3/min) flow. The temperature varied from room temperature up to 1000 °C.

The temperature programmed desorption (TPD) analyses were performed after, purging with helium flow (50 cm^3/min) up to 500 °C (10 °C/min). The sample was cooled to room temperature and reduced with pure H_2 (30 cm^3/min) up to 500 °C (10 °C/min), purged with helium flow for 30 min and cooled to room temperature.

NO was adsorbed by flowing 1% NO/He (50 cm^3/min) at room temperature for 15 min. Ethanol was uptake at room temperature flowing He through a saturator containing ethanol at 25 °C. Then, heated at 20 °C/min up to 500 °C in flowing helium (50 cm^3/min). The products were monitored using a quadrupole mass spectrometer (Balzers, PRISMA).

2.3. Catalytic activity

The experiments were performed in a glass microreactor at atmospheric pressure. Prior the reaction, the catalyst (ca. 140 mg) was pretreated in flowing helium (50 cm^3/min) at 500 °C for 1 h and reduced with pure H_2 (30 cm^3/min) at 500 °C for 1 h, purged with He for 30 min at the reduction temperature. The feed mixture for the NO reduction with ethanol consisted of 0.4% ethanol/0.6% NO in He (balance) at a flow rate of 250 cm^3/min (feed 1).

An oxygen mixture of 0.4% ethanol/0.6% NO/0.8% O_2 in He (balance) was prepared (feed 2). The input gas feed was 0.97% NO/He (AGA) and the ethanol/He mixture was introduced by flowing He through a saturator containing 99.999% pure ethanol (Merck) at 7.1 °C. The effluent was analyzed by gas chromatography (Varian CP-3900 with a TCD detector, Molsieve 5A and PoraBond-Q columns and cryogen).

3. Results and discussion

3.1. Characterizations

The Pd/ZrO_2 catalyst and the promoted sample presented adsorption isotherm that resemble a mesoporous material with H1 type hysteresis, as shown in Fig. 1. The samples have specific areas of 58 and 47 m^2/g, and average pore diameters of 21.7 and 19.8 nm, respectively.

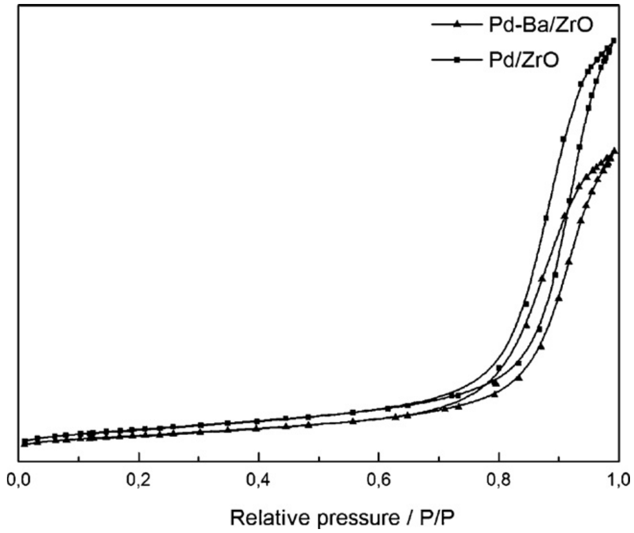

Fig. 1. Adsorption–desorption isotherm of the Pd/ZrO_2 and Pd–Ba/ZrO_2 catalysts.

The barium content was 14.3% and the mass loss was attributed to the impregnation procedure. The H_2 chemisorption results showed Pd dispersions of 37% and 30% for the unpromoted and promoted Ba catalysts, respectively.

The XRD spectra of ZrO_2 and the Pd–Ba/ZrO_2 samples are presented in Fig. 2, indicating the presence of monoclinic zirconia phase (JCPDS 34-1484) and $BaCO_3$ (JCPDS 45-1471), as shown in Fig. 2.

Fig. 3 displays the TG and DTA profiles with increasing temperature for Pd/ZrO_2 and Pd–Ba/ZrO_2. It shows water loss at 100 °C and a significant mass loss above 650 °C. In this temperature range the DTA analysis displays two endothermic peaks at 715 and 815 °C, which are attributed to the decomposition of different $BaCO_3$ phases, in accordance with Piacentini et al. [13]. The low thermal stability phase is due to the interaction of the carbonate with the alumina support which was decomposed between 400 and 800 °C while at 876 °C the weight loss is ascribed to the decomposition of crystalline phase, as shown by X-ray diffraction pattern in Fig. 2.

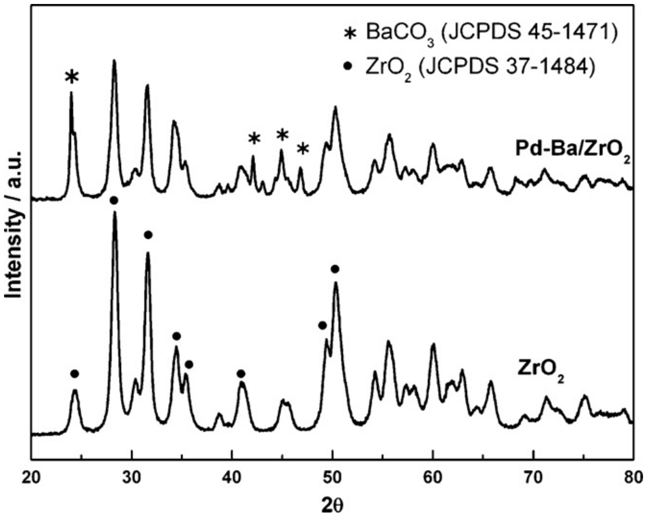

Fig. 2. XRD patterns of $BaCO_3$ and ZrO_2.

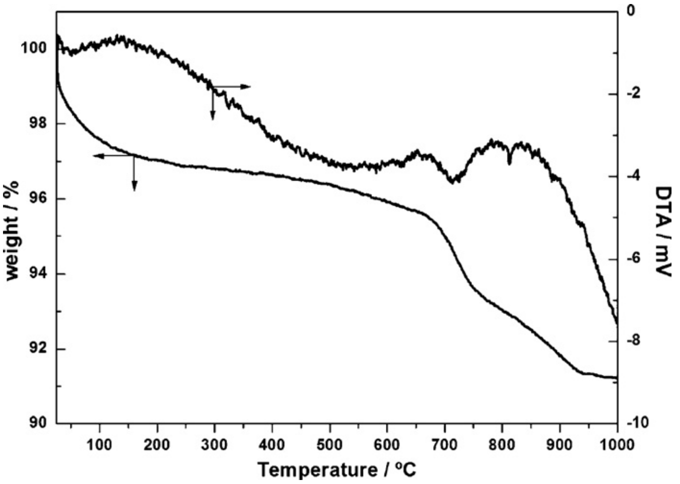

Fig. 3. Weight loss and DTA profiles for Pd–Ba/ZrO_2 catalyst.

3.2. Thermodesorption of NO

Fig. 4 shows the TPD profiles of NO on the Pd/ZrO_2 and Pd–Ba/ZrO_2 catalysts. The Pd/ZrO_2 displays a desorption peak of NO at 225 °C, with little formation of N_2, without N_2O and a shoulder of NO desorption around 330 °C without decomposition. On the other hand, the TPD profile of NO desorption on the Pd–Ba/ZrO_2 catalyst showed an opposite effect: NO desorption starting at 250 °C, with a shoulder at 340 °C and huge amount of N_2 formation between 180 and 330 °C, together with N_2O, centered at 200 °C. One observed also NO desorption at higher temperature above 450 °C, without N_2O or N_2.

The huge amount of N_2 formation on the Pd–Ba/ZrO_2 catalyst with a maximum peak at temperature around 240 °C suggests that barium promotes the NO decomposition. According to Piacentini et al. [13] barium acts probably as reservoir of NO. Beyond that, desorption of NO at higher temperature indicates strong interaction of NO with the catalyst.

TPD profiles of NO on these catalysts indicate that the major NO adsorption is reversibly. Only N_2 and N_2O were observed. However, on the Pd–Ba/ZrO_2 catalyst, the NO dissociation into N_2 as principal product must be accompanied with O_2 formation, according to following equations:

$$NO \rightarrow N_2 + \tfrac{1}{2}O_2$$

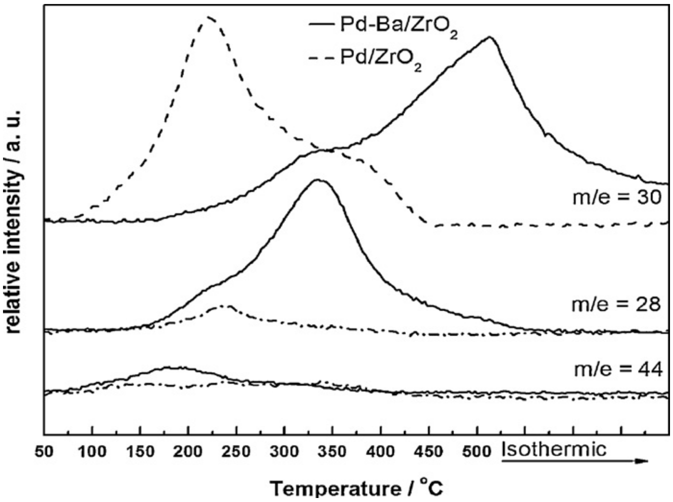

Fig. 4. TPD profile of NO adsorbed on Pd–Ba/ZrO_2 catalyst.

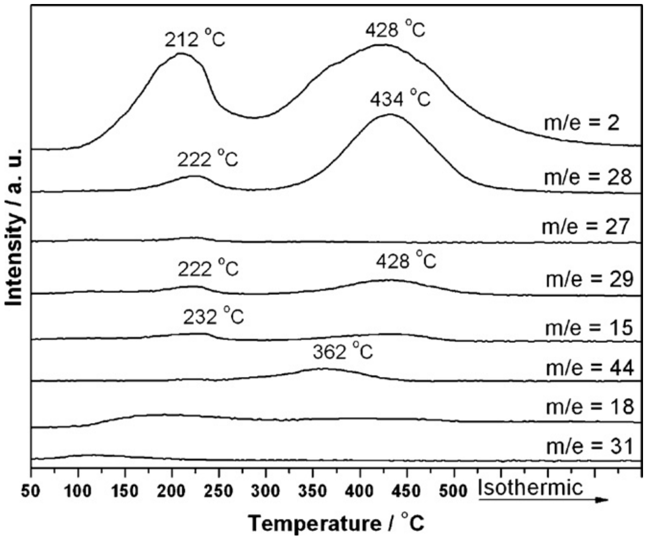

Fig. 5. TPD profile of ethanol adsorbed on Pd/ZrO_2 catalyst.

$$2NO \rightarrow N_2O + \tfrac{1}{2}O_2$$

and

$$2NO \rightarrow N_2 + O_2$$

$$NO \rightarrow N_{ads} + N_2O$$

However oxygen was not observed, which suggests both the oxidation of metallic Pd and the reaction of NO with O_2, as follows:

$$O_2 \rightarrow 2NO \rightarrow 2NO_2 \rightarrow N_2O + O^-$$

Probably the O^- is either stored in barium carbonate, and reacts at the surface transforming the carbonate in CO_2, which cannot be distinguished from N_2O in the TPD profile.

3.3. Thermodesorption of ethanol

Figs. 5 and 6 show the TPD profile of ethanol on Pd/ZrO_2 and Pd–Ba/ZrO_2. The profiles are very similar, however Pd sites are active for the decomposition of ethanol while Ba seems to blockade partially the active sites of Pd. One observe the formation of H_2 at 212 and 166 °C, respectively, which according to Bi et al. [14]

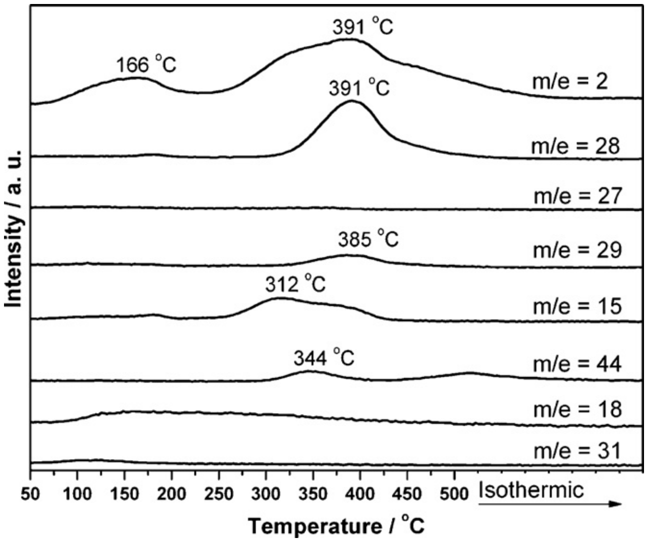

Fig. 6. TPD profile of ethanol adsorbed on Pd–Ba/ZrO_2 catalyst.

Table 1
Conversion and selectivity values.

Catalyst	Temperature (°C)	X_{NO} (%)	S_{N_2} (%)	$X_{ethanol}$ (%)	Selectivity of carbon species (%)				
					CO	Acetal	C1	C2	CO_2
Pd–Ba/ZrO_2 (feed 1)	250	100	48	77	1	3	57	0	39
	300	100	94	98	1	0	66	0	33
	350	100	100	100	1	0	77	0	22
Pd–Ba/ZrO_2 (feed 2)	250	10	38	93	3	4	14	0	79
	300	8	71	100	0	0	31	0	69
	350	4	79	100	0	0	10	0	90
Pd/ZrO_2 (feed 1)	250	18	22	41	21	5	65	0	9
	300	96	50	77	9	1	64	0	26
	350	100	71	96	10	0	51	1	38
Pd/ZrO_2 (feed 2)	250	10	1	100	0	0	16	0	84
	300	9	47	100	0	0	4	0	96
	350	7	42	100	0	0	8	0	92

X_{NO}: NO conversion; S_{N2}: N_2 selectivity; $X_{ethanol}$: ethanol conversion; acetal: acetaldehyde; C1: methane; C2: ethylene.

suggests the presence of atomic hydrogen combining to form H_2 molecule, while ethoxy species remain adsorbed. The peaks on the Pd–Ba/ZrO_2 are shifted to lower temperature about 40 °C, indicating the Ba may facilitate the decomposition of ethanol, weakening the adsorption of ethanol on the Pd sites. Besides the desorption of hydrogen there is at 312 °C formation of methane due to the combination between adsorbed methyl radicals and hydrogen at the surface, where the methyl radical origins from the rupture of intermediate species as follows:

$$CH_3CO_{(ads)} \rightarrow CH_{3(ads)} + CO_{(ads)}$$

It also explains the formation of CO ($m/e = 28$) at 390 °C.

The production of CO_2 ($m/e = 44$) can be related to the oxidation of methane, because the intensity of the relative signal of CO_2 increases and the intensity of the signal to methane ($m/e = 15$) decreases in the same range of temperature. Meanwhile, the formation of acetaldehyde ($m/e = 29$) at 385 °C is due to the ethanol dehydrogenation causing small change in the intensity of the signal ($m/e = 2$).

3.4. Activity tests

The results of NO reduction with ethanol are presented in Table 1 for both catalysts. It presents the conversion of NO and ethanol and the selectivity toward nitrogen and hydrocarbon compounds with different temperatures and feed conditions. In agreement with the TPD results, by comparing Pd/ZrO_2 with Pd–Ba/ZrO_2 there is a marked change. The promoted sample presented high NO conversion even at low temperature and an increasing selectivity to N_2.

According Skoglundh et al. [15], barium may decrease the inhibition effect caused by the presence of hydrocarbons in the NO adsorption. Besides, according to Nova et al. [16] NO_x can adsorb on $BaCO_3$ and react to form nitrates. The ethanol conversion increased, producing preferentially CH_4, CO_2, and a small fraction of CO with the absence of acetaldehyde above 300 °C.

As observed mainly methane and carbon dioxide are the main products, and therefore the oxidation may be occurring via acetate species, as suggested by Mello et al. [17].

A considerable reduction of NO conversion was observed for feed 2, where mainly the oxidation of ethanol to CO_2 and CH_4 formation via acetate species occurs. Since ethanol is preferentially oxidized, less ethanol is available for reduction of NO, suggesting that ethanol must be in excess to achieve high reduction levels. However, it also reduces the formation of N_2 which is attributed to the change of the oxidation state of palladium due to the partial oxidation of the metal, which hinders the NO dissociation on the metal, in agreement with TPD results.

Besides, oxygen modifies the ratio Pd/PdO diminishing also the capacity of hydrocarbon oxidation, as described by Yazawa et al. Error! Reference source not found [18]. Oxygen facilitates the formation of nitrates and the oxidation of ethanol, but reduces the NO molecules for the reduction of ethanol.

As described by Tuttlies et al. [19] based on core shrinking model when barium carbonate is transformed in barium nitrate during storage the molar volume of nitrate is higher and it difficult the access to palladium sites, lowering the capacity of reduction. Beyond that, there is a marked promoting effect of barium, resulting in a significant increase in the selectivity of N_2 and reduction of acetaldehyde, but did not affect the selectivity, prevailing CH_4 and CO_2.

4. Conclusion

The addition of barium on Pd/ZrO_2 catalyst does not modify the porous structure or the dispersion of the active phase. The X-ray diffraction results indicate the existence of monoclinic zirconia and barium carbonate which was confirmed by thermogravimetric analysis.

The catalytic results showed that the Pd–Ba/ZrO_2 catalyst presented higher capacity of NO_x reduction for feed 1, without oxygen, than the unpromoted catalyst. Beyond that barium promoted a significant increase of selectivity to N_2, in accordance with TPD results of NO.

Most important is that barium lowered the formation of acetaldehyde and does not provoke significant modification in the selectivity of ethanol, whose main products are CH_4 and CO_2.

The effect of O_2 in the NO_x reduction with ethanol changed markedly the reduction process due to the partial oxidation of the metal, hindering the NO dissociation with lower selectivity to methane.

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