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NO_x Reduction by Ethanol on Pd/Sulphated Zirconia

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Abstract The NO reduction by ethanol was studied on palladium catalyst supported on sulphated zirconia. Temperature programmed desorption of NO and ethanol (TPD) and temperature programmed surface reaction (TPSR) analyses as well as catalytic tests in reducing and oxidizing conditions (O_2 presence), besides diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) showed the formation of intermediate species during the reaction, such as ethoxy species that reacted forming ethylene. Besides dehydrogenate formed adsorbed acetate species, which than decompose and/or react with hydroxyls of the support. The sulphated zirconia support increased the acid sites with the formation of strong Brönsted sites, favoring the formation of ethoxy species. Acetate species also react with NO adsorbed on Pd forming N_2, N_2O, CO and CO_2. The excess of O_2 favored ethanol oxidation to CO_2, consequently less ethanol was available to react with NO_x.

Keywords NO_x reduction · Sulphated zirconia · Palladium · Ethanol · Desorption programmed temperature · DRIFTS

1 Introduction

The atmospheric pollution is one of the largest problems in the world causing damages to the environment and human health. Among the pollutants, compounds like NO_x (NO and NO_2) deserve special attention, because it contributes to the formation of acid rain, smog and ground level ozone [1].

Alcohol mixed in gasoline as fuel for vehicles was thought for better control of air pollution. Ethanol reduces the emission of olefins, aromatics, complex hydrocarbons, SO_x, monoxide carbon and others gas that contribute for the greenhouse effect [2]. The use of ethanol as fuel together with new technologies is responsible for the development of new engines (flex fuel) [3].

However, the use of ethanol, for instance, may increase the direct emission of aldehydes (acetaldehyde and formaldehyde) and also unburned alcohol. Apart from their potential carcinogenic effects, these new emission products may react in the atmosphere to form other toxic compounds and also contribute to the formation of urban smog [4, 5]. Therefore, these facts must be taken into account when projecting and testing catalytic system with the purpose of automotive pollution control.

The selective catalytic reduction (SCR) of nitrogen oxide (NO_x) 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 air/hydrocarbon high ratio [6]. The palladium catalysts supported on acidic materials, in particular, Pd/sulphated zirconia presented excellent performance for the NO_x reduction with methane in the presence of excess of oxygen [6–11]. These results awakened the interest of the current research to use palladium catalyst supported on sulphated zirconia for the NO_x reduction by ethanol.

There was a growth in research using ethanol as reductant for the SCR of NO_x, but in the case of sulphated catalysts it is an innovation. Recently, the reduction of NO by ethanol on palladium catalysts supported on NaZSM5

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and HZSM5 zeolites was studied [12]. Results showed that NaZSM5 and HZSM5 present different amounts of Lewis and Brönsted acid sites, which affect strongly the carbon production distribution, but not the nitrogen selectivity. NO reaction with ethanol in the presence of oxygen occurs only over the metal and is independent of the acid sites [12].

The main goal of the present work is to study the NO_x reduction by ethanol on Pd/sulphated zirconia catalyst. The adsorption and desorption properties of NO and ethanol besides the catalytic tests for NO + ethanol reaction in reducing and oxidizing conditions were studied. The oxidizing mixture was obtained in the presence of excess oxygen. In particular, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analyses was studied to identify the formation of intermediate species in the reaction path.

2 Experimental

2.1 Preparation of the Support and Catalyst

The sulphated zirconia (SZ) support was prepared using a mass of $Zr(OH)_4$ suspensed in deionized water and addition of $(NH_4)_2SO_4$. After stirring for 2 h at room temperature the resulting mixture was decanted and the remaining solid was dried at 110 °C for 24 h. Finally, the resulting sulphated zirconia was calcined for 5 h at 550 °C, at a heating rate of 1 °C min^{-1}. The palladium on sulphated zirconia (SZ) was prepared by dry impregnation using an aqueous solution of $Pd(NH_3)_4(NO_3)_2$. The sample was dried at 110 °C for 24 h and calcined up to 500 °C at a heating rate of 5 °C/min and air flow rate of 50 cm^3 min^{-1}. This sample was nominated Pd/SZ.

2.2 Characterization

The elemental chemical analyses of the samples (Table 1) was performed by X-ray fluorescence (XRF) using a Rigaku spectrometer, RIX 3100 model apparatus. The specific area (BET) was measured by N_2 adsorption using an ASAP 2010 (Micromeritics) equipment (Table 1). Before analyses, the samples were degassed for 24 h at 300 °C under vacuum.

The temperature programmed desorption (TPD) analyses was carried out on a system coupled to a mass quadrupole spectrometer (Balzers, PRISMA). The samples were pretreated under He flow at 500 °C for 30 min and cooled to room temperature. Either NO or ethanol was adsorbed at room temperature with a continuous flow of 1% NO/He or ethanol/He mixtures. The ethanol/He mixture was obtained by passing helium through a saturator containing ethanol at room temperature. After adsorption, TPD measurements were carried out by heating the samples at 20 °C min^{-1} up to 500 °C, under He flow. The products were continuously monitored by mass spectrometer.

Table 1 Results of loading metallic and textural characterization

Samples	Pd loading (wt %)	SO_4 loading (wt %)	BET area (m^2g^{-1})
SZ	–	3.7	159
Pd/SZ	0.5	3.7	137

The temperature programmed surface reaction (TPSR) was performed in the same apparatus. The sample was purged with helium (50 cm^3 min^{-1}) up to 500 °C (10 °C min^{-1}) and cooled to room temperature. Ethanol was adsorbed at room temperature until saturation. After adsorption and purge with He flow a mixture 1% NO/He (50 cm^3 min^{-1}) was flown rising the temperature at 20 °C min^{-1} until 500 °C.

The diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed on a Nexus 470 (Thermo Nicolet) FTIR, equipped with an in situ diffuse reflection chamber and high sensitivity MCT/A detector cooled by liquid nitrogen and a high temperature chamber fitted with ZnSe windows (Spestra-Tech). Before analyses, the sample was treated with He flow (30 cm^3 min^{-1}) at 500 °C for 30 min, cooled to room temperature (30 °C) under helium and recorded with the reference spectrum. Ethanol was adsorbed on the sample at different temperatures (30, 130, 250 and 320 °C) with an ethanol/He mixture flow during 5 min, using a saturator containing ethanol at room temperature and He flow (30 cm^3 min^{-1}). Then, 1% NO/He (30 cm^3 min^{-1}) flow in the chamber for 2 min and was closed during 15 min. Finally, temperature was increased with He flow. This process was repeated at 130, 250 and 320 °C.

Catalytic tests of NO with ethanol were performed in a glass microreactor at atmospheric pressure. Reaction products were analyzed by gas chromatography (Varian 3900) using a Molecular Sieve 5A and a Porabond Q column and He as carrier gas, equipped with a thermal conductivity detector and cryogenic system. NO and NO_2 were measured separately in a TESTO 350 XL equipped with electrochemical cell. Prior to the reaction, the samples were pretreated with He at 500 °C for 30 min and then cooled to the initial reaction temperature (250 °C). Two feed mixtures were used for the reaction: a reducing mixture consisting of 0.6% NO + 0.4% ethanol balanced with He and an oxidizing mixture consisting of 0.6% NO + 0.4% ethanol + 1.2% O_2. The reaction temperature varied between 250 and 320 °C. The total flow rate was 250 cm^3 min^{-1} and the weight sample was 140 mg. The ethanol/He mixture was obtained by passing helium through a saturator containing ethanol at 7 °C.

3 Results

3.1 NO-TPD

Figures 1 and 2 display the TPD profiles of NO on sulphated support (SZ) and Pd/SZ catalyst, respectively. Notice great NO desorption on SZ with a small peak at 100 °C, a shoulder at 230 °C and a peak at 308 °C. N_2O was observed around 126 and 359 °C. On Pd/SZ catalyst NO desorbed at 113 and 305 °C, while N_2O appears at 113 °C. However, O_2 and N_2 were not detected on the samples.

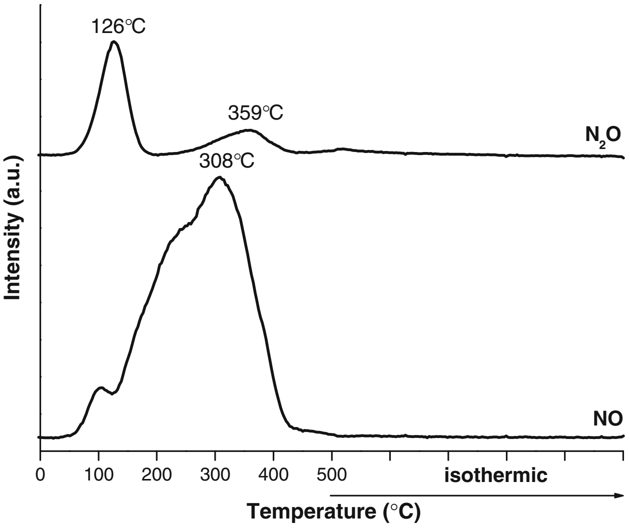


Fig. 1 TPD profile of NO adsorbed on SZ support

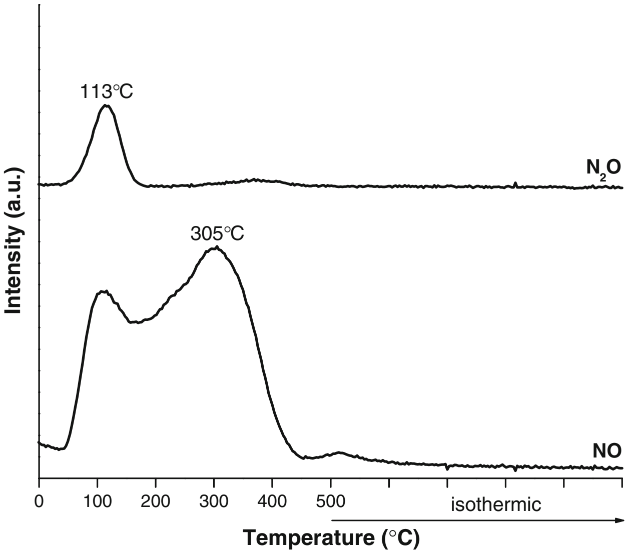


Fig. 2 TPD profile of NO adsorbed on Pd/SZ catalyst

3.2 TPD of Ethanol

Figures 3 and 4 display the TPD profiles of ethanol on SZ and Pd/SZ catalysts, respectively. Ethanol desorbed on the support (SZ) exhibiting a maximum peak at 142 °C, accompanied by signals $m/e = 44$, 29, 28, 27, 15 and 2. The signals $m/e = 44$, 29 and 15 are identical to the desorption profile of mass $m/e = 31$, which can be attributed to the fragmentation of ethanol. The desorption profiles of masses $m/e = 28$ and 27 at 240 °C are relative to the ethylene formation due to the ethanol dehydration on acid sites of the support. The addition of a metal on SZ

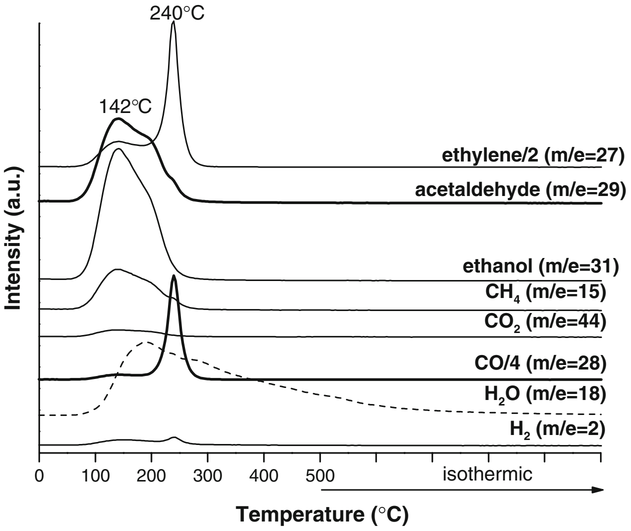


Fig. 3 TPD profile of ethanol adsorbed on SZ support

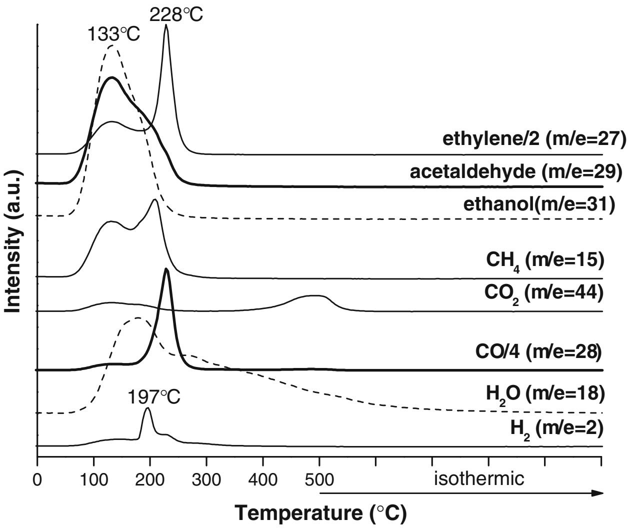


Fig. 4 TPD profile of ethanol adsorbed on Pd/SZ catalyst

support favored the decomposition reaction of ethanol, as observed from the higher intensity of methane ($m/e = 15$) and hydrogen ($m/e = 2$) peaks. At higher temperature, above 400 °C, CO_2 desorbed ($m/e = 44$) and is assigned to the decomposition of more stable adsorbed species.

3.3 TPSR of Ethanol + NO

Figure 5 shows TPSR profiles on the support (SZ), which are very similar to the TPD profiles of ethanol (Fig. 3). NO was not consumed during TPSR experiments. As seen in TPD the NO adsorption is reversibly over the support. Ethanol adsorption on the support is predominant, transforming it into adsorbed species, impeding NO adsorption at the surface at higher temperatures. TPSR profile showed NO desorption between 50 and 300 °C, with simultaneous formation of different products. It suggests that there is a competition of ethanol and NO at the surface of the support.

The TPSR profiles on the Pd/ZS catalyst are presented in Fig. 6. At lower temperatures we observed dehydration, dehydrogenation and decomposition reactions, very similar to the TPD results, forming ethylene, acetaldehyde and methane, CO and H_2, respectively. The signals $m/e = 29$ and 15 are fragments of ethanol, acetaldehyde and methane. At higher temperatures the decomposition of ethanol was not observed. It differs from the TPD results of ethanol, where decomposition was only favored in the presence of palladium. TPSR showed NO consumption at 339 and 464 °C with the formation of N_2 and/or CO and N_2O and/or CO_2.

3.4 DRIFTS

Figure 7a shows the DRIFTS spectrum of ethanol adsorption at room temperature on Pd/SZ catalyst. Spectrum (a) shows the C–O stretching region with bands at 1,926, 1,712, 1,564, 1,481, 1,450, 1,315, 1,255, 1,151, 1,078 cm^{-1} and an intense negative band at 1,370 cm^{-1}. According to the literature [13–16], ethanol adsorbs at the surface of metal oxides by scission of O–H bond, forming ethoxy species. Therefore, the bands at 1,481, 1,450, 1,151 and 1,078 cm^{-1} can be assigned to ethoxy species. The band at 1,255 cm^{-1} has been assigned to ethanol molecularly adsorbed on Lewis acid sites over the support [15]. The bands appearing at 1,564 and 1,315 cm^{-1} suggest that a further oxidation of ethoxy species takes place, producing acetate and/or carbonate species [17], while the negative band at 1,370 cm^{-1} is due to the perturbation the of sulphate groups by the adsorbed species [18]. The bands observed between 2,200 and 1,700 cm^{-1} have been attributed to CO adsorption on metal particles [19]. The bands between 1,900 and 1,700 cm^{-1} were assigned to bridge or multi-coordinated adsorbed CO [20]. However, the bands at 1,926 and 1,712 cm^{-1} can not be related to CO adsorption on metal particles at room temperature and was not identified.

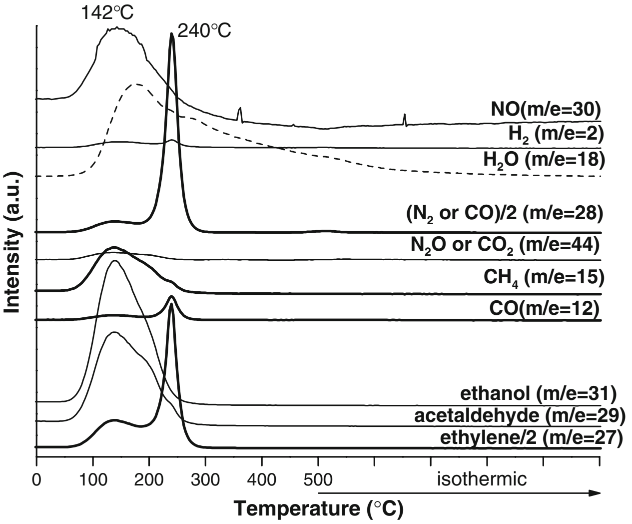


Fig. 5 Ethanol/NO-TPSR profile on SZ support

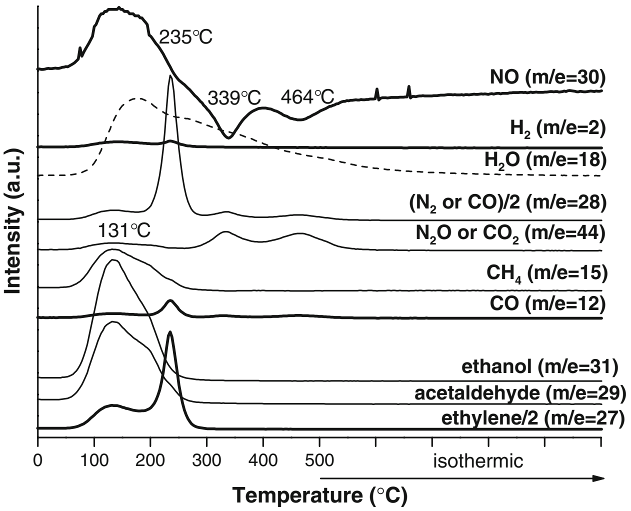


Fig. 6 Ethanol/NO-TPSR profile on Pd/SZ catalyst

Figure 7b shows the spectrum of ethanol adsorption on Pd/SZ. Spectrum (*a*) displays the C–H stretching region with bands at 2,976, 2,931, 2,900 and 2,881 cm^{-1}, which can be attributed to the ethoxy species [17, 21, 22].

Figure 7 also exhibits the spectra of NO reaction with adsorbed ethanol at different temperatures (spectra (*b*)–(*h*)). The ethoxy bands of spectrum (*a*) (2,976, 2,931, 2,900, 2,881, 1,481, 1,151 and 1,078 cm^{-1}) decreased after reaction with NO and heating from 30 to 320 °C. The bands at 1,926, 1,712 and 1,255 cm^{-1} decreased also, with the appearance of new bands at 1,658, 1,539, 1,342 cm^{-1} and increasing of the band intensity at 1,450 cm^{-1}. CO_2 is formed, as observed in the spectrum (*f*). Species, which were formed on spectra (*b*)–(*h*) are not clear and probably

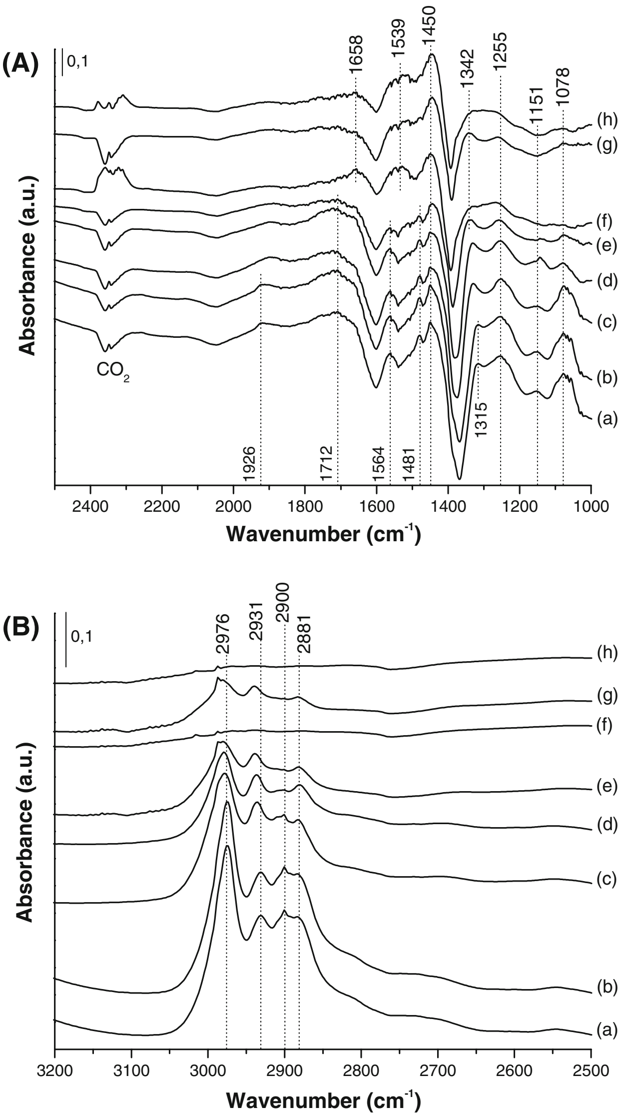


Fig. 7 DRIFTS spectra of Pd/SZ catalyst. (*a*) ethanol/He flow at room temperature (5 min), (*b*) closed chamber at room temperature in presence of NO (15 min), (*c*) ethanol/He flow at 130 °C (5 min), (*d*) closed chamber at 130 °C in presence of NO (15 min), (*e*) ethanol/He flow at 250 °C (5 min), (*f*) closed chamber at 250 °C in presence of NO (15 min), (*g*) ethanol/He flow at 320 °C (5 min), (*h*) closed chamber at 320 °C in presence of NO (15 min)

are overlapping bands. Therefore, band at 1,539 cm^{-1}, which overlaps band at 1,564 cm^{-1}, can be attributed to nitrate and nitrite species [23], besides acetate and/or carbonate species. The band at 1,342 cm^{-1} is related to acetate and/or carbonate species. Surface species or intermediate of aldehydes appeared at 1,658 cm^{-1} [24], which can be also attributed to nitrate [18] and acetate [16] species.

3.5 Catalytic Tests

3.5.1 NO + Ethanol Reaction − Reducing Condition

Table 2 presents results for reducing condition on Pd/SZ catalyst. NO conversion increased with temperature and ethanol conversion varied between 58 and 68% in this temperature range. The catalyst presented good selectivity to nitrogen. For carbon species one observed ethylene, acetaldehyde and small amounts of CO_2. More ethylene than acetaldehyde was observed in all temperature range on Pd/SZ. Since more consumption of ethanol was observed than required to reduce NO, the greater amount of ethylene formation is due to the dehydration of ethanol. Ethylene and acetaldehyde formation were observed due dehydration and dehydrogenation reactions of ethanol, in accordance with TPD and TPSR results. NO does not react over the support unlike ethanol, which suggests that the NO reaction with ethanol occurs essentially on palladium sites.

3.5.2 NO + Ethanol + O_2 Reaction − Oxidizing Condition

Table 3 shows the results under oxidizing conditions in presence of oxygen. The production of CO_2 was observed and increased with temperature, which is related to the oxidation of ethanol. On the other hand, NO_x, which represents the mixture of NO + NO_2 in the presence of oxygen, exhibited low conversion at 320 °C. The addition

Table 2 Catalytic tests results on Pd/SZ catalyst in NO reduction by ethanol in reducing conditions

0.6% NO + 0.4% ethanol

Catalyst	Temperature (°C)	Conversion (%)		Selectivity N species (%)		Selectivity of carbon species (%)				
		NO	Ethanol	N_2	N_2O	CO	CO_2	Ethylene	Acetaldehyde	CH_4
Pd/SZ	250	4	58	91	9	0	0	84	16	0
	300	14	65	58	42	0	5	83	12	0
	320	22	68	44	56	3	13	74	10	0

Table 3 Catalytic tests results on Pd/SZ catalyst in NO reduction by ethanol in the presence of O_2

0.6% NO + 0.4% ethanol + 1.2% O_2

Catalyst	Temperature (°C)	Conversion (%)		Selectivity N species (%)		Selectivity of carbon species (%)				
		NO_x	Ethanol	N_2	N_2O	CO	CO_2	Ethylene	Acetaldehyde	CH_4
Pd/SZ	250	6	69	82	18	0	0	79	21	0
	300	11	100	59	41	2	60	28	3	7
	320	12	100	59	41	0	83	11	1	5

O_2 in the feed favored the N_2 formation despite the low NO_x conversion.

Similar results were obtained by Mello et al. [16, 25] using different oxygen contents in the NO + ethanol reaction for the Pd/Al_2O_3 catalyst. With low O_2 content no significant differences were observed. However, with increasing O_2 the major adsorbed ethanol on alumina was oxidized to CO_2 and CO, without parallel reaction on the support, which is in good agreement with these results between 300 and 320 °C. Results showed that with 0.4% O_2, the NO_x conversion decreased drastically. There are two possibilities: NO_x reacting with ethanol with the formation of acetate species, or direct oxidation of ethanol. With O_2 part of NO is transformed in NO_2; this reacts easily with ethanol. Ethanol oxidation increases with oxygen concentration, increasing also CO_2 and disfavoring the NO_x reaction with ethanol, decreasing also the NO_x conversion.

4 Discussion

TPD profiles of NO on the support and the catalyst indicate that majority of NO adsorption is reversibly. Besides, O_2 and N_2O were observed on the Pd/SZ catalyst, suggesting that NO molecules are dissociated in atoms and recombined at the surface, according to Eqs. 1–4.

$$NO_{g.} \rightarrow NO_{ads.} \tag{1}$$

$$NO_{ads.} \rightarrow N_{ads.} + O_{ads.} \tag{2}$$

$$O_{ads.} + O_{ads.} \rightarrow O_2 \tag{3}$$

$$N_{ads.} + NO_{ads.} \rightarrow N_2O \tag{4}$$

g, gas; ads., adsorbed.

According to the literature [26] the NO-TPD profiles on γ-alumina showed NO desorption at two different temperatures: 248 °C and around 500 °C, which were associated to different NO adsorption forms on alumina. N_2O and N_2 released during desorption were attributed to the NO dissociation and oxygen in the vacancies. With increasing temperature the excess of oxygen in the network is desorbed and N adsorbed atoms are rearranged, releasing N_2 and N_2O. We observed also H_2O desorption (not shown) suggesting rearranging of hydroxyls groups over the support.

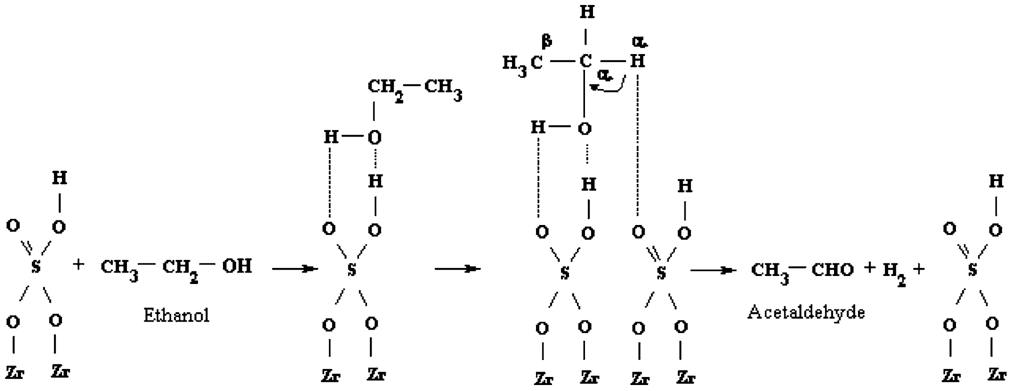
TPD analyses of ethanol suggest the presence of acids sites on the support because of the dehydration of ethanol and formation of ethylene. With Pd it is decomposed to CO, CH_4 and H_2, in agreement with the literature [16, 25, 27]. Cordi and Falconer [27] observed dehydration on alumina, with ethylene the main product. With Pd/alumina they observed simultaneously dehydrogenation with the formation of acetaldehyde and H_2, however, three times more hydrogen than acetaldehyde, and claim that the adsorbed acetaldehyde may react, forming carbon species at the surface. CO_2 is desorbed above 530 °C, probably due to the decomposition of acetate.

Results suggests that part of the ethoxy species adsorbed on support may migrate to the palladium sites and decompose to CO, CH_4 and H_2, and part can react producing more stable adsorbed species that are the precursors of CO and CO_2 at higher temperatures [27]. Above at 450 °C these species are decomposed and/or may react with hydroxyls of support, forming CO, CO_2 and H_2, which are in agreement with Mello et al. [16] on Pd/alumina catalyst. Besides, DRIFTS results confirmed the formation of ethoxy species and a negative band at 1,370 cm^{-1}, which is attributed to the perturbation the of sulphate groups by the adsorbed species [18]. A large and very small band observed at 2,747 cm^{-1} and could be assigned to S–OH groups, which are probably strong Brönsted acid sites as observed by Martins [28] studying superacid catalysts. Bands between 1,370 and 1,027 cm^{-1} are related to S=O of sulfate and bisulfate groups. Therefore, the adsorptions of NO and ethanol can be sketched as follows, supporting also the reaction path for NO and ethanol proposed by Mello et al. [16].

As noticed NO and ethanol are competing on palladium sites and ethanol on free acid sites of the support. Therefore,

$$NO + Pd \rightarrow NO^{*} \tag{5}$$

Ethanol + support, as sketched below:



(6)

According to the proposition of Mello et al. [16] acetaldehyde may be adsorbed on Pd sites and form acetate species, which than react with adsorbed NO at the surface as follows:

$$8NO^* + 2HNO^* + 2CH_3COO^* \xrightarrow{-[O]} 5N_2 + 2CO_2 + 4H_2O + 2^* + 10Pd \quad (7)$$

*, site; [O], surface oxygen.

Therefore, the sulfated zirconia surface contributes to the formation of strong Brönsted acid sites, which favor the formation of ethoxy and acetate intermediates for the reaction. It can also favor the dehydration of ethanol to ethylene, increasing the ethanol conversion.

When NO is reacting with ethanol in presence of O_2 (Table 3) ethylene and acetaldehyde are low, increasing CO_2 due to the total oxidation of ethanol, which is independent of the support, occurring mainly on Pd sites.

5 Conclusion

Pd/SZ catalyst was studied for the reduction of NO by ethanol. TPD of ethanol showed the presence of acids sites over the sulphated zirconia support, while Pd sites are responsible for ethanol decomposition. Moreover, TPSR results showed that when ethanol is first adsorbed on the support do not migrate over palladium sites, decreasing methane, CO and H_2 formation due to the preferential adsorption of NO on the Pd sites. DRIFTS results confirm the presence of intermediates during the NO + ethanol reaction. The sulphated zirconia increases the acidity with the formation of strong Brönsted acid sites, favoring the formation of ethoxy and acetate species. With palladium the dehydrogenation favors the formation of intermediate species such as, acetate species, which than decompose or react with hydroxyls of the support forming CO and CO_2. The acetate species may react with NO adsorbed on Pd sites with the formation of adsorbed species that decompose to N_2, N_2O, CO and CO_2. The excess of O_2 in the NO + ethanol feed favors total oxidation increasing CO_2, but decreases the NO_x conversion.

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