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NO_x reduction by ethanol on Pd/zeolites-effect of oxygen

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Abstract The reduction of NO by ethanol on palladium catalysts supported on NaZSM-5 and HZSM-5 zeolites was studied. Temperature programmed techniques, such as desorption of ethanol, NO and surface reaction (TPSR) analyses, besides NH_3 (NH_3–TPD), as well as, FTIR after pyridine adsorption were used to accomplish reaction products and surface properties. Results show that NaZSM5 and HZSM5 present different amounts of Lewis and Brönsted acid sites, which affect strongly the carbon product 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.

Keywords NO reduction · ZSM5 · Palladium · Ethanol · Desorption programmed temperature · Pyridine-IR

1 Introduction

The atmospheric pollution is one of the largest problems in the world causing damages to the environment and human health. Automobiles contribute intensely in the atmospheric pollution. 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 was mixed in gasoline as fuel for automotive vehicles and it was thought for better control of air pollution. The addition of ethanol reduces the emission of olefins, aromatics, complex hydrocarbons and SO_x [2]. However, the use of ethanol, for instance, may increase the direct emission of aldehydes (acetaldehyde and formaldehyde) and also unburned alcohol to the environment, which is a disadvantage due to the carcinogenic effects of those products [1]. Therefore, these facts must be taken into account when projecting and testing catalytic system with the purpose of automotive pollution control.

Metallic catalysts supported on zeolites were investigated intensively for selective catalytic reduction (SCR) of NO_x with methane and among them the palladium presented excellent activity in NO reduction even in the presence of steam [1].

Palladium catalysts are very active for NO reduction with methane, however in the presence of oxygen the selectivity depends on the support [3, 4]. Loughran e Resasco [4] observed that with non acidic supports SiO_2 the combustion of methane occurs preferentially, while NO does not react. However, Pd catalysts supported on acidic materials, such as HZSM5, H-mordenite and sulfated zirconia present great selectivity for NO reduction. Therefore, the effectiveness of Pd was related to the acidity of the support for the reaction NO–CH_4 [5].

Some studies are reported in the literature for NO_x reduction with ethanol as reductant agent [6–13]. Mello et al. [6] studied the PdO–MoO_3 catalysts supported on Al_2O_3 in this reaction and oxygenated compounds. This work [6] revealed that for reduction of NO by ethanol, the oxidation occurs, probably, on palladium sites. For the NO + ethanol reaction a mechanism was suggested, where adsorbed ethanol is transformed in ethoxy species, forming then acetate species reacting with NO adsorbed species on palladium sites.

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Salgado et al. [8] studied the NO reduction with ethanol on palladium and molybdenum catalysts supported on HZSM5 zeolite. After the addition of Mo on Pd/HZSM5, an promoting effect on the catalytic ativity was achieved at high temperatures. However, the selectivity into N_2 on Pd and Pd–Mo catalysts practically did not present significant differences.

A multistep mechanism has been elucidated for reduction of NO_x in the presence of added ethanol over Ag/γ-Al_2O_3 at 320 °C [9]. Under these conditions, ethanol principally reacts with oxygen to form acetaldehyde. Surface acetate ions, which are formed from adsorbed acetaldehyde, react with NO_2 to yield nitromethane (intermediate). In contrast, NO_x reduction with ethanol over Ag/γ-Al_2O_3 at 200 °C is inefficient, because surface acetate ions are much less reactive at 200 °C than at 320 °C. At 200 °C, the dominant pathway for ethanol oxidation is reaction with NO_2, producing ethyl nitrite, which decomposes into a number of products, including N_2O, which is stable under reaction conditions.

Finally, NO reduction by oxygenated compounds was studied over Pt/Al_2O_3 catalyst [13], which showed that primary alcohols are good reducers; however, for 50% conversion the temperature T_{50} °C was the less active under all other oxygenated reducers.

The main goal of the present work is to study the NO reduction by ethanol on Pd/NaZSM5 and Pd/ZSM5 catalysts containing different types of acidic sites, Lewis and Bronsted, respectively as main sites. The effect of oxygen on the reduction of NO by ethanol in function of reaction temperature was also investigated.

2 Experimental

2.1 Preparation of Catalysts

HZSM5 was obtained by ion-exchange of NaZSM5 zeolite (SAR = 37.7) using a suspension of NaZSM5 with 25% NH_4Cl solution at 50 °C and pH 4.5, under constant stirring during 30 min. Then, the mixture was filtered and washed with 10% NH_4Cl solution for three times and washed with deionized water. The solid was dried in mufle at 110 °C for 24 h and calcined at 550 °C during 6 h.

Pd/NaZSM5 e Pd/HZSM5 were prepared by ion-exchange with NaZSM5 and HZSM5, respectively, using an aqueous solution of $Pd(NH_3)_4(NO_3)_2$ (Aldrich) with 1% (wt) Pd content. The ion-exchange was performed at 80 °C during 24 h, under constant stirring. The sample was filtered, washed with deionized water, dried at 110 °C for 24 h and then calcined under flowing air (300 cm^3/min) at 400 °C for 2 h.

2.2 Characterization

The elemental chemical analysis was performed by X-ray fluorescence (XRF) using a Rigaku spectrometer, RIX 3100 model apparatus.

The specific surface area was measured by N_2 adsorption measurements (BET method), using a Micromeritics ASAP 2000 apparatus. Before analysis, the samples were degassed for 24 h at 200 °C under vacuum.

The total acidity of the zeolites and catalysts were measured by temperature programmed desorption of NH_3 (NH_3–TPD). Approximately, 100 mg was pretreated under He flow at 350 °C for 1 h, reduced with 1.7% H_2/Ar flow at 500 °C and degassed with He flow. Ammonia was adsorbed at 150 °C and degassed with He flow to remove weakly adsorbed molecules. Desorption was performed varying the temperature from 150 °C to 700 °C.

Pyridine adsorption measurements were performed by infrared spectroscopy aiming to determine the nature of acids sites (Brönsted and Lewis). The spectra were obtained in a Perkin–Elmer model System 2000 FTRI apparatus. The concentrations of Brönsted and Lewis acids sites were calculated from the intensity bands located at 1540 and 1450 cm^{-1}, respectively, using as molar extinction coefficients (ε) 0,059 $cm^2/\mu mol$ for Brönsted acids and 0,084 $cm^2/\mu mol$ for Lewis acids, applying the Lambert–Beer equations [14–16].

Temperature programmed desorption (TPD) unit for NO and ethanol analyses consists of a glass microreactor and an oven with controlled temperature programmer. The gas effluents were analyzed by a quadrupole mass spectrometer (Balzers, PRISM). The samples were pretreated with He flow at 400 °C for 30 min. After cooling to room temperature the catalysts were reduced in H_2 flow at 450 °C for 1 h, then purged with He flow for 30 min at 450 °C and cooled to room temperature. NO was admitted to the reactor with 1% NO/He flow. In the case of ethanol the adsorption was performed by flowing He through a saturator containing absolute ethanol maintained at room temperature. After adsorption the samples were purged with He, followed by desorption, rising the temperature up to 500 °C at 10 °C/min.

Temperature programmed surface reaction (TPSR) analyses was performed in the same unit and same procedure of pre-treatment and reduction. After adsorption of ethanol a gas mixture of 1% NO/He, was flown through the reactor at a heating rate of 10 °C/min, from room temperature up to 500 °C and products were accomplished by mass spectrometry.

Catalytic reaction of NO with ethanol was studied in a differential flow reactor, using 0.3% NO with 0.2% ethanol balanced with He and total flow rate of 250 cm^3/min at 320 °C for 50 min before each analysis [6–8]. With oxygen the feed composition was 0.6% NO, 0.4% ethanol, 1.2% O_2 and total flow rate of 250 cm^3/min. On this condition the catalyst performances were evaluated at each temperature (255, 300 and 320 °C) after stabilization for 50 min. The reaction was performed in a glass microreactor at atmospheric pressure. Reaction products were analysed by gas chromatography (Varian 3900) equipped with a thermal conductivity detector and cryogenic system. NO and NO_2 were measured in a TESTO 350 XL equipped with a electrochemical cell.

3 Results

Textural analysis and compositions are shown in Table 1. The BET area and micropore volumes of HZSM5 and Pd/HZSM5 are larger than of NaZSM5 and Pd/NaZSM5 samples. The incorporation of metal on the zeolites did not change the structure.

3.1 Acidity—NH_3 and Pyridine

The total acidity was measured and Fig. 1 shows the desorption profile of NH_3 on NaZSM5 zeolite exhibiting two peaks at 350 and 477 °C. The HZSM5 zeolite displayed two peaks of desorption with maximum temperatures at 294 and 450 °C. The acidity was calculated at different intervals of temperature, accounting the NH_3 desorbed. Table 2 presents the total acidity and acid strength of the samples. The amount of NH_3 desorbed on the HZSM5 zeolite is larger than on NaZSM5 (Table 2). According to Li et al. [17] the desorption around 307 °C would be assigned to weak acid sites, due to Lewis sites, while that located around 357–407 °C and 467–507 °C are assigned to medium and strong sites, respectively, which are attributed to the adsorption on Brönsted acids sites.

Pyridine infrared spectra are shown in Fig. 2 and presented in Table 3 confirm the nature and the amounts of acids sites.

The results of NH_3 desorption (Table 2) indicate a great concentration of acid sites (97.2%) on HZSM5 mainly located rat high temperatures (450 °C), in agreement with the pyridine IR results, presenting 11.1 μmol/mg of pyridine desorbed from the Brönsted acids sites. The weak acid sites of HZSM5 account 2.8% (Table 2) and are located at 294 °C, desorbing 1.4 μmol/mg of pyridine, which is attributed to Lewis acids sites, in accordance with Li et al. [13]. Requejo et al. [18] studied the acidic properties of zeolites with different Si/Al ratios, using TPD of NH_3 and IR of pyridine. They observed two desorption peaks on the HZSM5 zeolite at 200 °C and 500 °C. Results showed prevailing desortpion at higher temperatures on all samples, which was attributed to the interaction of NH_3 with strong Brönsted acid sites, in accordance with our results on HZSM5.

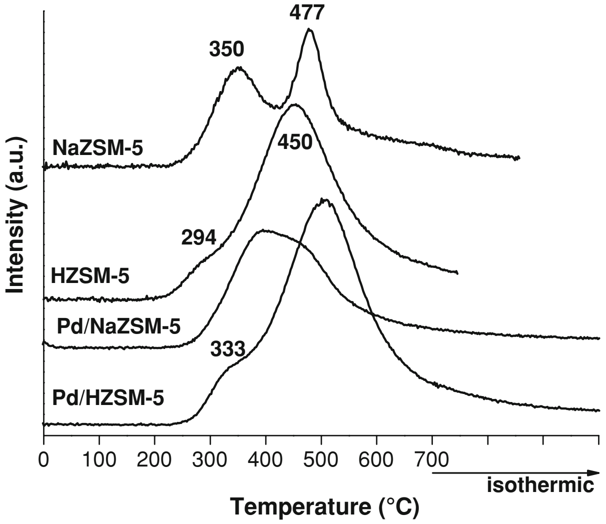

Fig. 1 NH_3–TPD profile

Table 2 NH_3–TPD results

Samples	Consumption (μmol NH_3/gcat.)	NH_3 Desorption (°C)	Acid force (%)	
			Peak 1	Peak 2
NaZSM5	640.6	350 and 477	43.6	56.4
HZSM5	728.7	294 and 450	2.8	97.2
Pd/NaZSM5	745.1	–	–	–
Pd/HZSM5	854.6	333 and >500	4.2	95.8

Table 1 Results of loading metallic and textural characterization

Samples	Loading metallic theoretical (wt.%)	Loading metallic real (wt.%)	BET area (m^2/g)	Microporous area (m^2/g)	Microporous volume (cm^3/g)
NaZSM5	–	–	328	325	0.15
HZSM5	–	–	379	378	0.18
Pd/NaZSM5	1	1.1	333	326	0.15
Pd/HZSM5	1	0.9	367	382	0.18

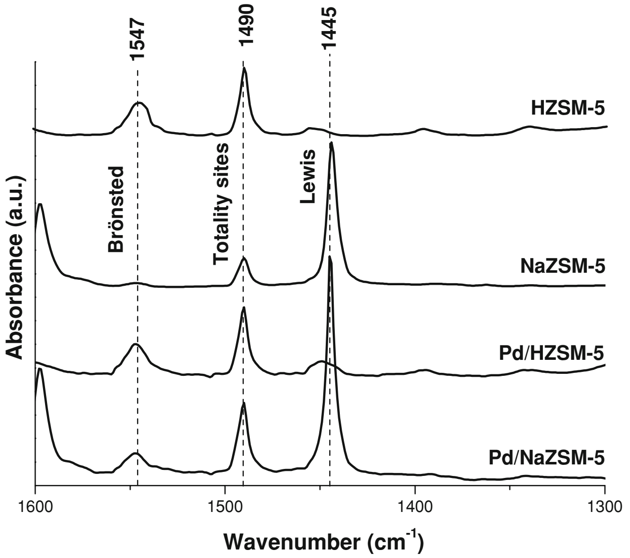

Fig. 2 IR spectra of pyridine adsorbed

Table 3 Pyridine-FTIR results

Samples	Lewis acids sites (µmol/mg)	Brönsted acids sites (µmol/mg)	Totality of acids sites (µmol/mg)
NaZSM5	12.5	0.2	12.7
HZSM5	1.4	11.1	12.5
Pd/NaZSM5	15.5	3.6	19.1
Pd/HZSM5	3.2	9.8	13.0

Different results were observed on NaZSM5, as shown in Table 2 and Fig. 2, displaying two peaks at 350 and 477 °C, but equivalent concentration of weak and strong acid forces, respectively, 43.6% and 56.4%. On the contrary, the IR results of pyridine presented greater amount of Lewis acids sites (12.5 µmol/mg) than Brönsted sites (0.2 µmol/mg), in contradiction with the TPD of ammonia results and Li's observation [17]. This contradiction is probably due to different techniques, because ammonia is a strong basic molecule and easily adsorbed on acids sites, while pyridine is a weak basic molecule and adsorbed specifically on acids sites. Indeed, the HZSM-5 zeolite is more acidic than the NaZSM5 (728.7 and 640.6 µmol $NH_3/g_{cat.}$, respectively), exhibiting more strong Brönsted acids sites, and on the contrary the NaZSM5 presents more Lewis acid sites.

TPD of NH_3 profiles and the IR spectra of pyridine on Pd/HZSM5 and Pd/NaZSM5 presented also large amounts of ammonia desorption (854.6 µmol $NH_3/g_{cat.}$ and 745.1 µmol $NH_3/g_{cat.}$, respectively). The addition of Pd into HZSM5 and NaZSM5 modify total acidity and the concentration of Bronsted and Lewis acid sites of the supports, mainly of the NaZSM5. Noteworthy is that the Pd/NaZSM5 catalyst presented a larger amount of Lewis acids sites, and a larger amount total acid sites (19.1 µmol/mg) (Table 2).

3.2 Thermodesorption of NO–TPD

The profiles of temperature programmed desorption after adsorption of NO on NaZSM5 and HZSM5 zeolites are shown in Figs. 3 and 4, respectively. Desorption peaks of m/e = 30, 28 and 44 were observed on NaZSM5 around 117 °C and at 500 °C, corresponding to NO desorption, N_2 and N_2O formation, respectively, while on HZSM5 only

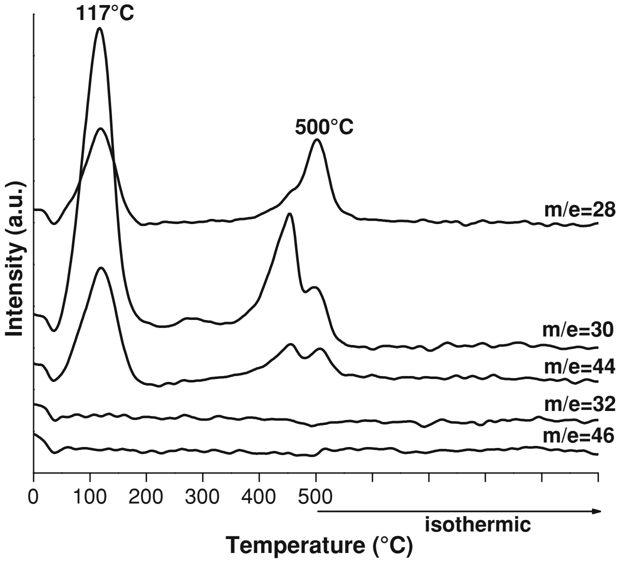

Fig. 3 TPD profile of NO adsorbed on NaZSM5 zeolite

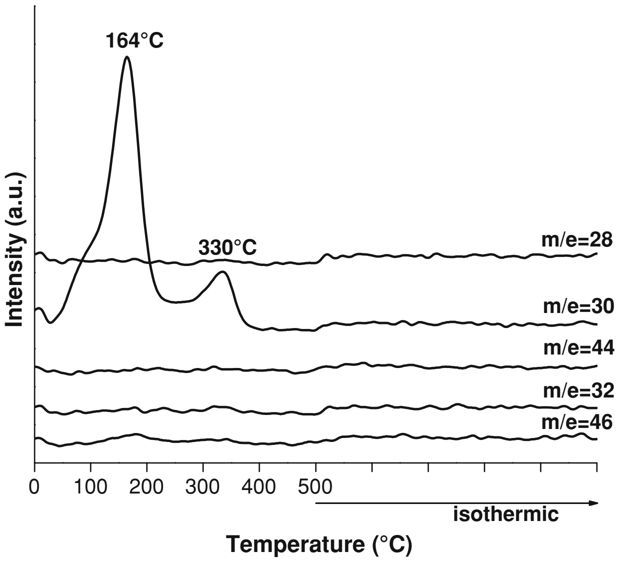

Fig. 4 TPD profile of NO adsorbed on HZSM5 zeolite

desorption of NO, suggesting that NO was not decomposed. Figures 5 and 6 show the TPD profiles on Pd/NaZSM5 and Pd/HZSM5 catalyst, respectively. NO decomposes at low temperature, since the mass m/e = 30 is not a fragment of m/e = 44, as observed on NaZSM5 (Fig. 3). The desorption peak at 279 °C (m/e = 30) is attributed to NO adsorption on Pd species. Figure 6 shows that NO desorption on Pd/HZSM5 at low temperature is similar to HZSM5 (Fig. 4). At higher temperature, above 400 °C, a second NO desorption peak was observed, which can be associated to NO adsorbed on palladium.

3.3 Thermodesorption of Ethanol

Temperature programmed desorption profiles of ethanol on Pd/HZSM5 and HZSM5 are shown in Figs. 7 and 8, respectively. These profiles show ethylene formation on HZSM5 (m/e = 27), which are attributed to the dehydration of ethanol (Eq. 1); dehydrogenation of ethanol (m/e = 31) in acetaldehyde (m/e = 29) at 250 °C (Eq. 2). The simultaneous formation of CO (m/e = 28), CH_4 (m/e = 15) and H_2 (m/e = 2), are assigned to the decomposition of ethanol (Eq. 3). Figure 9 displays the desorption

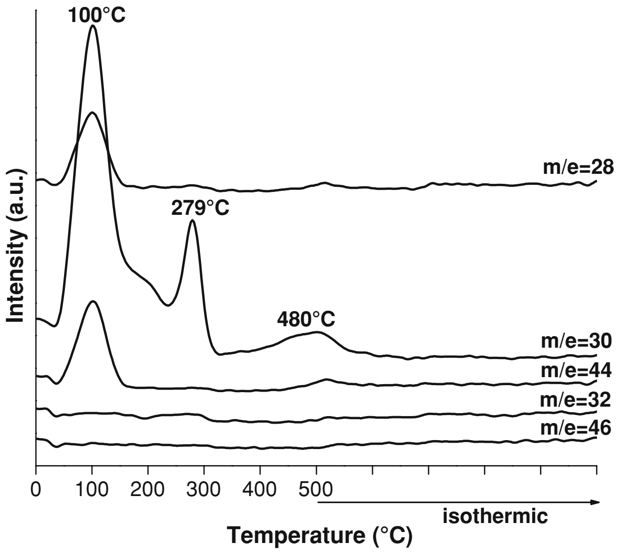

Fig. 5 TPD profile of NO adsorbed on Pd/NaZSM5 catalyst

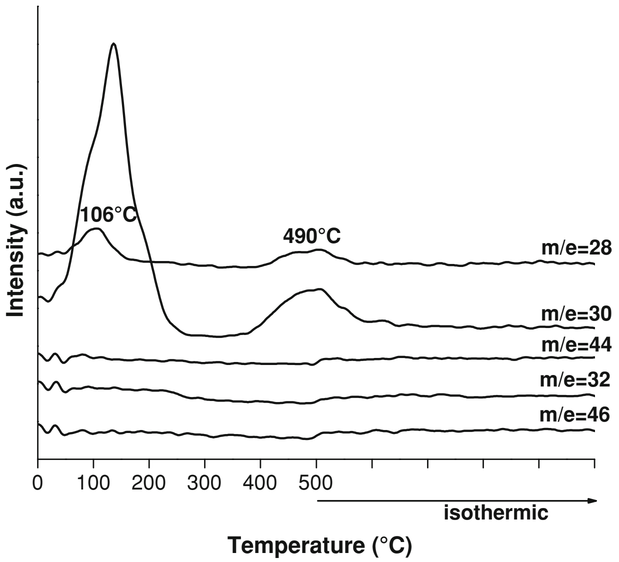

Fig. 6 TPD profile of NO adsorbed on Pd/HZSM5 catalyst

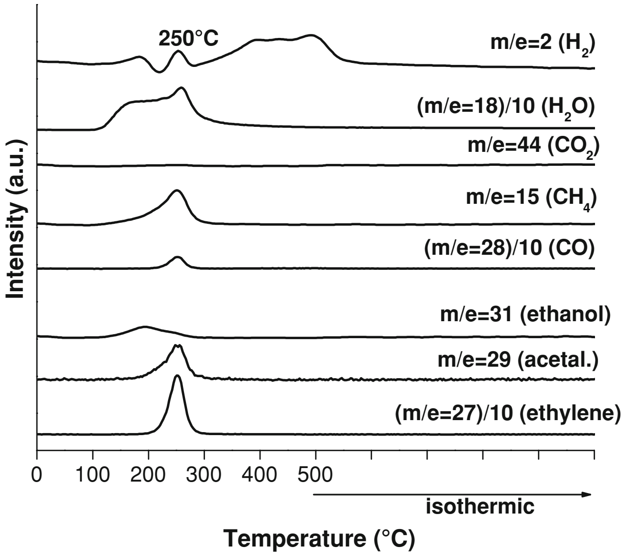

Fig. 7 TPD profile of ethanol adsorbed on Pd/HZSM5 catalyst for: m/e = 44 (carbon dioxide), m/e = 31 (ethanol), m/e = 29 (acetaldehyde), m/e = 27 (ethylene), m/e = 18 (water), m/e = 15 (methane), m/e = 28 (carbon monoxide) and m/e = 2 (hydrogen)

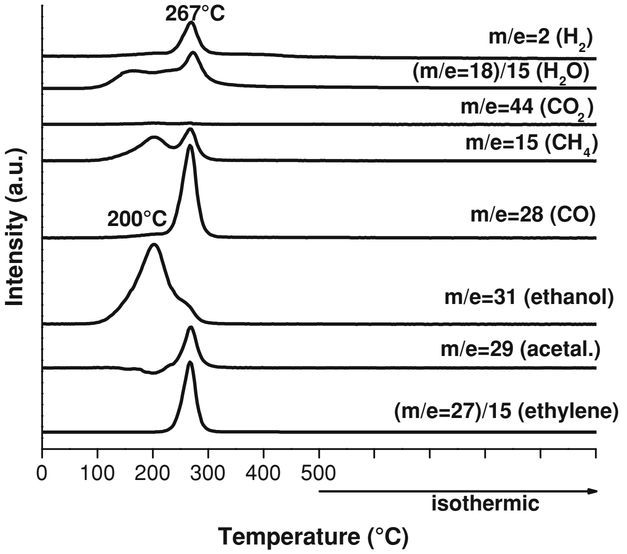

Fig. 8 TPD profile of ethanol adsorbed on HZSM5 zeolite

profiles of ethanol on NaZSM5, as well as ethylene desorption, but much less than on HZSM5, which, as expected, is attributed to the stronger acids sites on HZSM5. Figure 10 presents the TPD profiles on Pd/NaZSM5, showing desorption of ethanol between 96 and 304 °C, with simultaneous formation of ethylene (m/e = 27), acetaldehyde (m/e = 29), CO (m/e = 28), CH_4 (m/e = 15) and H_2 (m/e = 2), and a maximum peak at 267 °C. Hydrogen was also observed but only above 300 °C.

$$\text{Dehydration: } C_2H_5OH \rightarrow C_2H_4 + H_2O \tag{1}$$

$$\text{Dehydrogenation: } C_2H_5OH \rightarrow C_2H_4O + H_2 \tag{2}$$

$$\text{Decomposition: } C_2H_5OH \rightarrow CH_4 + CO + H_2 \tag{3}$$

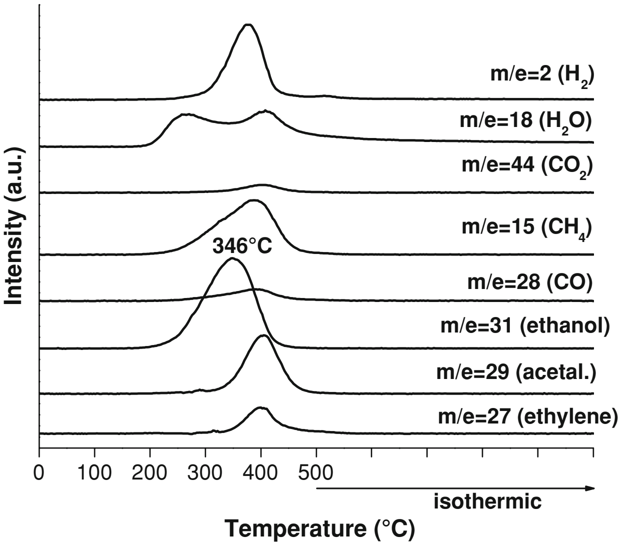

Fig. 9 TPD profile of ethanol adsorbed on NaZSM5 zeolite

Cordi and Falconer [19] observed during ethanol desorption on Pd/alumina more hydrogen than acetaldehyde and claim that acetaldehyde remains adsorbed at the surface and decomposes producing carbon species. Above 530 °C, small amounts of CO_2 desorb, due to the decomposition of acetaldehyde [19]. Results show that up to 500 °C only H_2 desorbs.

The amount of ethylene on HZSM5 is larger than on NaZSM5. With the incorporation of palladium into HZSM5 the acidity decreased and consequently reduces ethylene formation. In contrast, the Pd/NaZSM5 is more acidic than NaZSM5 and forms higher amount of ethylene that NaZSM5.

3.4 Temperature Programmed Surface Reaction of Ethanol with NO–TPSR

TPSR results show that NO-ethanol profiles on HZSM5 and NaZSM5 are very similar to the TPD profiles of ethanol and suggest that the reaction of NO with ethanol do not occurs.

Results of Ethanol + NO on the Pd/HZSM5 catalyst are displayed in Fig. 11, and show that they are also similar to the TPD profiles of ethanol (Fig. 7). Consumption of NO (m/e = 30) begins around 400 °C, with simultaneous formation of products masses m/e = 44, 28 and 12. Mass m/e = 15 is probably attributed to methane or CH_3 fragment, due to the reaction of NO in the gas phase with intermediate adsorbed carbon species at the surface, such as acetate species [7], producing CO (m/e = 28 and 12) and/or CO_2 (m/e = 44, 28 and 12), besides N_2O (m/e = 44 and 30) and/or N_2 (m/e = 28). It seems that ethanol and NO compete for the same sites during the adsorption but

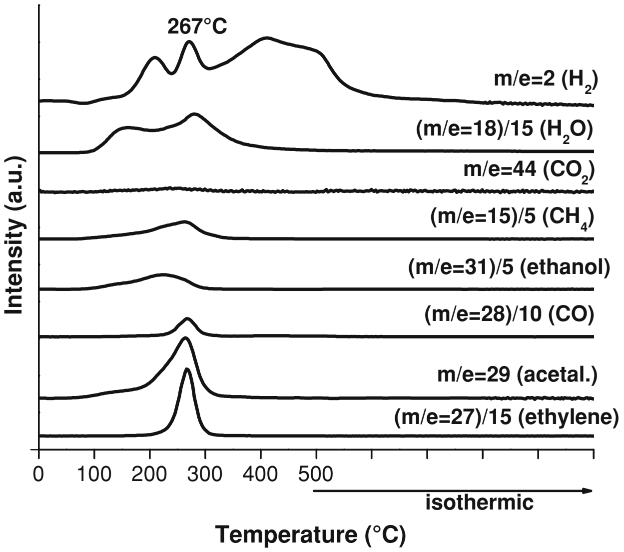

Fig. 10 TPD profile of ethanol adsorbed on Pd/NaZSM5 catalyst

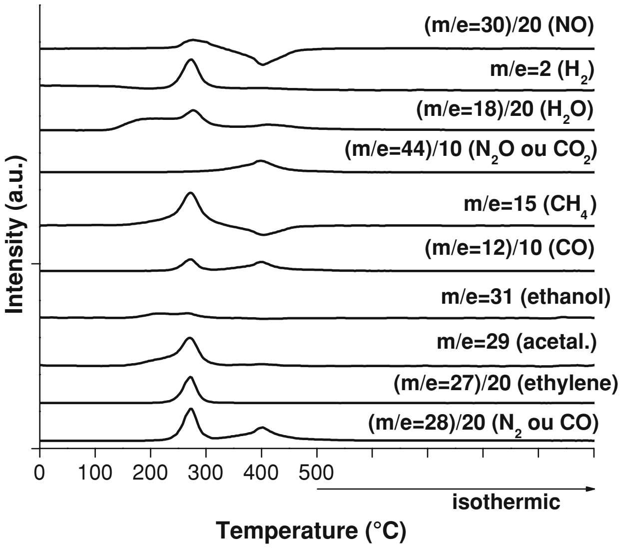

Fig. 11 NO—ethanol TPSR profile on Pd/HZSM5 catalyst

once ethanol is adsorbed at room temperature it is necessary to desorb and/or dissociate ethanol to permit adsorption and dissociation of NO. The consumption of CH_4 (m/e = 15) starts at 300 °C, indicating reaction of NO with methane, with the formation of products masses m/e = 44, 28 and 12 (Fig. 12).

Figure 13 shows the results for Pd/NaZSM-5, indicating dehydrogenation and decomposition reactions of ethanol. The maximum consumption of NO (m/e = 30) and CH_4 (m/e = 15) was observed at 356 °C with simultaneous formation of masses m/e = 44, 28 and 12). These results are similar for Pd/HZSM5, producing CO (m/e = 28 and 12) and/or CO_2 (m/e = 44, 28 and 12), besides N_2O (m/e = 44 and 30) and/or N_2 (m/e = 28).

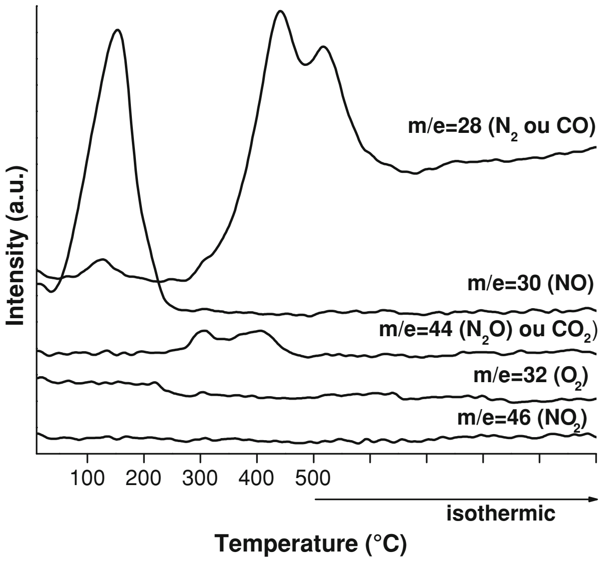

Fig. 12 NO—CH_4 TPSR profile on Pd/HZSM5 catalyst

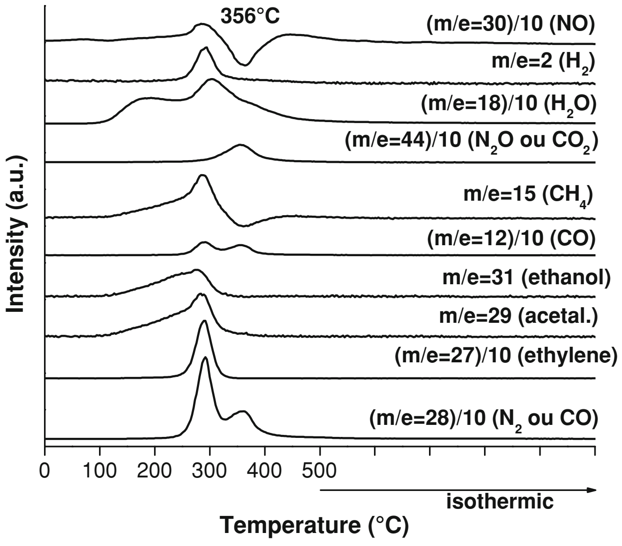

Fig. 13 NO—ethanol TPSR profile on Pd/NaZSM5 catalyst

3.5 Catalytic Tests of NO Reduction with Ethanol

Table 4 presents the results of reduction of NO by ethanol on Pd/NaZSM5 and Pd/HZSM5. Pure zeolites NaZSM5 and HZSM5 are inactive, as shown in Table 4, in accordance with TPSR results. The conversion of ethanol is 100% on HZSM5 zeolite, transforming ethanol into ethylene on acids sites and a small fraction of ethanol in CO_2. However, NaZSM5 converted only 62% of ethanol to ethylene, CO_2 and acetaldehyde.

The conversion of ethanol is greater as expected, because of its reaction with NO, in accordance with Eq. 4 (Table 4). This is attributed to the parallel reactions of ethanol with the support occuring simultaneous with the dehydration of ethanol.

$$6NO + C_2H_5OH \rightarrow 3N_2 + 2CO_2 + 3H_2O \tag{4}$$

The Pd/NaZSM5 catalyst exhibited greater conversion of NO than Pd/HZSM5, respectively, 52% and 35%,. The selectivity to nitrogen products was similar, but the selectivity to carbon species forming acetaldehyde was greater on Pd/NaZSM5.

Table 5 presents the results of NO reduction in the presence of oxygen for different temperatures. Both samples present high conversions of ethanol but similar conversions of NO_x ($NO + NO_2$) and similar selectivity to N_2 for different temperatures. The carbon distribution products changed with the temperature. Low temperature favored the formation of ethylene, while high temperature the formation of CO_2. Noteworthy is the comparison of both catalysts at 320 °C with and without oxygen. In the absence of oxygen the selectivity of N_2 and N_2O are equivalent, while, with oxygen the selectivity was preferentially toward N_2 on both catalysts. On the other hand, without oxygen the carbon products favored preferentially the formation of ethylene, but less acetaldehyde and CO_2, while oxygen converted all to CO_2, independent of the zeolite. It also disfavored the NO_x conversion, prevailing the N_2 production.

Table 4 Catalytic tests results of the reduction of NO by ethanol, at 320 °C in reducing conditions

Samples	Conversion (%)		Selectivity (%)					
			N species		C species			
	NO	Ethanol	N_2	N_2O	CO	CO_2	Acet.	Ethyl.
NaZSM5	0	62	0	0	0	20	33	47
HZSM5	0	100	0	0	0	17	0	83
Pd/NaZSM5	52	100	49	51	0	3	13	84
Pd/HZSM5	35	100	49	51	0	29	0	71

Acet. = acetaldehyde and Ethyl. = ethylene

Table 5 O_2 influence in the reduction of NO by ethanol

Samples	T (°C)	Conversion (%)		Selectivity (%)						
				N species		C species				
		NO_x	Ethanol	N_2	N_2O	CO	CO_2	Acet.	Ethyl.	CH_4
Pd/NaZSM5	250	5	96	94	6	12	15	15	44	14
	300	26	100	80	20	0	94.7	0	0.4	4.9
	320	30	100	76	24	0	99.3	0	0.7	0
Pd/HZSM5	250	0.2	100	98	2	0	0	6	94	0
	300	25	100	74	26	0	94.5	1.2	4.3	0
	320	27	100	78	22	0	95	0	5	0

Acet. = acetaldehyde and Ethyl. = ethylene

4 Discussion

It seems that the acidity may affect the NO reduction with ethanol. The Pd/HZSM5 indicate dehydration while the Pd/NaZSM5 dehydration and dehydrogenation. Palladium on zeolites has been reported by Nishizaka and Misono showing high catalytic activity for CH_4 SCR [20]. They claim that NO_2 reacts on Pd/zeolite catalyst much faster than NO. Therefore NO reduction proceeds via the formation of NO_2 and that zeolitic acid sites are needed to oxidize NO into NO_2 and activate CH_4 by a synergic effect with the palladium sites on zeolite. Moreover, from the viewpoint of the state of palladium on Pd/HZSM5 compared with Pd/NaZSM5, the acidity is needed to keep the palladium sites dispersed and active for the reaction [21].

There is a correlation between acidity and NO reduction. Table 4 presents the results of NO reduction with ethanol for pure NaZSM5 and HZSM5 and with the corresponding Pd catalysts. Notice that the supports are inactive for NO reduction with ethanol, but very active for ethanol decomposition, converting 62% and 100% of ethanol on NaZSM5 and HZSM5, respectively, under similar conditions. However, the product distribution is different on both cases. On NaZSM5 the concentrations are: ethylene (47%), CO_2 (20%) and C_2H_4O (33%), while on HZSM5 ethylene was 83% and, CO_2 17%. TPD of ethanol indicate CH_4, water and small amounts of CO. This suggests shift (Eq. 5) and reforming of methane reactions (Eq. 6) on NaZSM5 and in parallel decomposition of CO into CO_2 (Eq. 7), according following reactions:

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{5}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{6}$$

$$2CO \rightarrow C + CO_2 \tag{7}$$

On the other hand, HZSM5 produced CO_2 and ethylene, represented by reactions (1), (5) and (7).

Although both non-palladium samples have almost the same total acidity, as shown from pyridine-FTIR results (Table 3), the Lewis and Brönsted acid sites are quite different. In NaZSM5 there are a big amount of Lewis sites, while in HZSM5 there are a big amount of Bronsted acid sites. The Bronsted acidic sites favor the dehydration of ethanol forming ethylene and in the contrast the Lewis acidic sites on NaZSM5 favor the decomposition of ethanol and CH_4, also observed by TPD of ethanol, following reactions (5) and (6) favoring shift and the reforming of methane. HZSM5 favors also the Bourdouart reaction (7) with the formation of CO_2, evidencing the abscense of CO which is transformed into CO_2, as shown in Table 4.

Noteworthy is the dehydrogenation reaction occurring on the NaZSM5, usually attributed to the presence of a metal. It suggests that the Lewis acid sites, absent on the HZSM5 sample, are active for the dehydrogenation reaction in the NaZSM5.

The effect of the metal (Pd) of both samples on the reduction of NO_x by ethanol shows that only the metal activates NO, converting (Table 4) to N_2 and N_2O. This may be attributed to the decomposition of NO, as evidenced by TPD of NO. Indeed, the following reactions may occur:

$$NO_g \rightarrow NO_{ads} \tag{8}$$

$$NO_{ads.} \rightarrow N_{ads.} + O_{ads.} \tag{9}$$

$$O_{ads.} + O_{ads.} \rightarrow O_2 \tag{10}$$

$$2N_{ads.} \rightarrow N_2 \tag{11}$$

$$NO_{ads.} + N_{ads.} \rightarrow N_2O \tag{12}$$

We observe that the total acidity of both catalysts are similar, however, after reduction the total acidity of the Pd/NaZSM5 catalyst increased from 12.7 μmol/mg to 19.1 μmol/mg, in accordance with Loughran and Resasco

[22], indicating that during the reduction protons are introduced on NaZSM5. Indeed, the Bronsted acid sites increased 18-fold with the addition of Palladium, while the Lewis acid sites not significantly, confirming the introduction of protons in the NaZSM5 zeolite. The Bronsted and Lewis acid sites on HZSM5 and Pd/HZSM5 did not change too much. However, the product distribution of Pd/NaZSM5 and Pd/HZSM5 changed markedly, as observed from the results presented in Table 4, where CO_2 decreased abruptly 10-fold and acetaldehyde 3 times on Pd/NaZSM5, compared to NaZSM5, while ethylene increased at twice. It suggests that NO and ethanol are competing for the metallic Pd and Lewis acid sites simultaneously. Thus, since the NO decomposition on the Pd sites releases O_2 (Eq.10) and because ethanol adsorbs on both sites the partial oxidation of ethanol is favored occurring the following reactions.

$$6NO + C_2H_5OH \rightarrow 3N_2 + 2CO_2 + 3H_2O \tag{13}$$

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O \tag{14}$$

Also acetaldehyde was observed at lower temperature on Pd/HZSM5 and Pd/NaZSM5, which according to Yeom et al. [23] indicate that NO_2 is an intermediate molecule for the reaction with ethanol, occurring the following reduction reactions:

$$2NO_2 + C_2H_5OH \rightarrow C_2H_5ONO + HNO_3 \tag{15}$$

$$C_2H_5ONO \rightarrow C_2H_5O + NO \tag{16}$$

Remarkable is the effect of oxygen on the reduction of NO by ethanol at 320 °C. The conversion of NO_x decreases, forming preferentially N_2. The conversion of ethanol is 100% favoring in all cases CO_2, and no other carbon compounds. Therefore, it depends only of the PdO sites and not on the Lewis and Bronsted sites of the HZSM5 and NaZSM5, which are insensitive for this reaction in the presence of oxygen. The results suggest that in the presence of oxygen and ethanol the following reaction may occur:

$$2NO + C_2H_5OH + 2O_2 \rightarrow N_2 + 2CO_2 + 3H_2O \tag{17}$$

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O \tag{18}$$

5 Conclusions

The results of this study show that in NaZSM5 there are mainly Lewis acidic sites, in contrast in HZSM5 support mainly Bronsted acidic sites. After introduction of palladium ions in HZSM5 and NaZSM5 and their further reduction with H_2, the number of Bronsted acidic sites decrease slightly for HZSM5 and increase strongly (18 times) for NaZSM5. It is shown that NO react with ethanol only in the presence of metal and this reaction is not depended on the presence of acidic sites. The presence of oxygen in the reaction mixture favors the SCR of NO by ethanol with higher selectivity into N_2.

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