



## LOW TEMPERATURE HYDROGEN SELECTIVE CATALYTIC REDUCTION OF NO ON Pd/Al<sub>2</sub>O<sub>3</sub>

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Received November 5, 2010

Alumina supported Pd catalyst prepared by the incipient wetness impregnation method was tested at low temperatures (< 300°C) for the selective catalytic reduction of NO using hydrogen (NO H<sub>2</sub>-SCR). The catalyst was characterized by N<sub>2</sub> adsorption-desorption at -196°C, X ray powder diffraction and NO temperature programmed desorption. Pd/Al<sub>2</sub>O<sub>3</sub> (1 wt. % Pd) was tested at 5 different temperatures from 100 to 300°C, at a reactant ratio NO:H<sub>2</sub> = 1:1.25, and GHSV = 15,000 h<sup>-1</sup>. Both catalyst and reducing agent proved efficient under these reaction conditions. The reaction products of NO H<sub>2</sub>-SCR are N<sub>2</sub>, N<sub>2</sub>O and H<sub>2</sub>O. NO conversion is strongly dependent on the reaction temperature. Total NO conversion is reached at 150°C and above. N<sub>2</sub>O formation is also temperature dependent, the largest amount of it being formed at temperatures below 120°C. Working temperatures above 175°C lead to total N<sub>2</sub> selectivity. Formation of ammonia was not evidenced.

### INTRODUCTION

There is an ongoing interest regarding the removal of nitrogen oxides (NO and NO<sub>2</sub>) emissions from both mobile and stationary sources, due to their negative effects on the environment, in general, and on human health, in particular. Selective catalytic reduction (SCR) with adequate reducing agents is considered to be the best choice for the abatement of nitrogen oxides from the flue gases.<sup>1-3</sup> However, choice of the reducing agent is of great importance as it is desirable to control NO<sub>x</sub> emissions in such a way as to minimize the introduction or the production of a new pollutant. Thus, use of hydrogen as reducing agent is a reasonable alternative to other SCR techniques.<sup>4,5</sup> On the other hand, low temperature (T < 300°C) SCR is more advantageous due to reduced investment and operating costs.<sup>6</sup>

Basically, there are three types of catalysts that have been developed by now for SCR systems: (i) supported noble metal catalysts; (ii) metal oxides; and (iii) zeolites.<sup>2,7</sup> However, catalysts investigated for hydrogen SCR (H<sub>2</sub>-SCR) over the last two

decades make use of platinum group metals (PGM), no matter the supporting material, and were tested mainly for the reduction of NO<sub>x</sub> from vehicular exhaust. In case of industrial H<sub>2</sub>-SCR, Pt catalysts (Pt/La<sub>0.5</sub>Ce<sub>0.5</sub>MnO<sub>3</sub>,<sup>8</sup> Pt/MgO-CeO<sub>2</sub>,<sup>6,9</sup> Pt/La<sub>2</sub>O<sub>3</sub>,<sup>10</sup> Pt/SiO<sub>2</sub>,<sup>10</sup> Pt/TiO<sub>2</sub>,<sup>10,11</sup> Pt/CaO,<sup>10</sup> Pt/Ti-MCM-41, or Pt/Si-MCM-41<sup>12</sup>) and some Pd catalysts (Pd/SiO<sub>2</sub>, Pd/MgO, Pd/Al<sub>2</sub>O<sub>3</sub> with 2 wt.% Pd<sup>5</sup>) have been proved to be active for NO<sub>x</sub> reduction at temperatures below 300°C. Supported Pt catalysts were found to be very active for H<sub>2</sub>-SCR of NO, while supported Pd catalysts seem to present higher N<sub>2</sub> selectivity.<sup>10</sup>

The aim of this work is to test hydrogen SCR (H<sub>2</sub>-SCR) of NO at low temperatures on Pd/Al<sub>2</sub>O<sub>3</sub> (1 wt.% Pd) and to investigate the influence of the reaction temperature on the catalytic activity.

### RESULTS AND DISCUSSION

Impregnation of the prepared  $\gamma$ -alumina with Pd leads to a decrease of the total surface area (from 211.5 m<sup>2</sup>/g for Al<sub>2</sub>O<sub>3</sub> to 179.5 m<sup>2</sup>/g for Pd/Al<sub>2</sub>O<sub>3</sub>)

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and of the specific pore volume (from  $0.26 \text{ cm}^3/\text{g}$  for  $\text{Al}_2\text{O}_3$  to  $0.18 \text{ cm}^3/\text{g}$  for  $\text{Pd}/\text{Al}_2\text{O}_3$ ). The type IV adsorption – desorption isotherm (Fig. 1), as well as the relatively uniform pore size distribution with a medium diameter of  $35 \text{ \AA}$ , prove the catalyst as a mesoporous material (Fig. 2).

X ray powder diffraction pattern revealed that diffraction peaks are very broad for  $\text{Al}_2\text{O}_3$ , suggesting that the support is rather amorphous. The dimension of crystallites for  $\text{Al}_2\text{O}_3$  was evaluated using Scherrer's equation and we obtained  $D = 20 \text{ \AA}$ . For  $\text{Pd}/\text{Al}_2\text{O}_3$  sample,

reflections of Pd correspond to the planes (111) at  $40^\circ$ , (200) at  $46^\circ$ , (220) at  $68^\circ$  and (211) at  $82^\circ$  (Fig. 3). No reflection corresponding to PdO was observed.<sup>13</sup> Crystallite dimension for the deposited Pd on the alumina support was evaluated as being  $D = 542 \text{ \AA}$ . This significant difference between the crystallite dimensions of Pd, and  $\text{Al}_2\text{O}_3$  respectively, is due to the great difference in their cristalinity. Moreover, the amorphous state of the support is a limitation for the determination of its crystallite dimension.

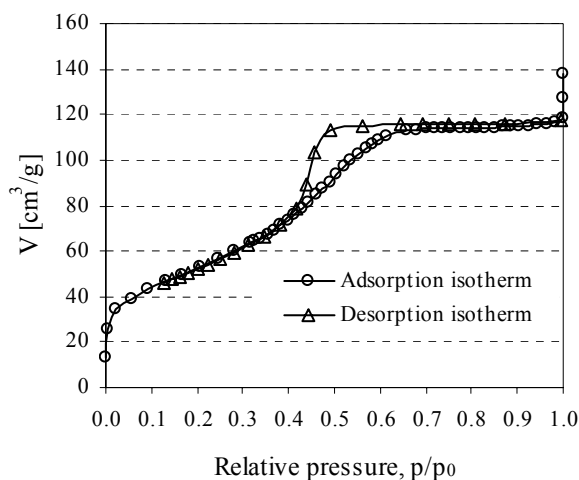


Fig. 1 – Adsorption-desorption isotherm of  $\text{N}_2$  for  $\text{Pd}/\text{Al}_2\text{O}_3$ .

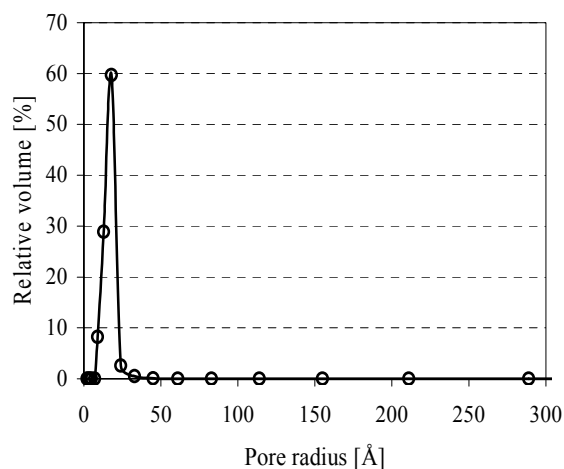


Fig. 2 – Pore size distribution for  $\text{Pd}/\text{Al}_2\text{O}_3$ .

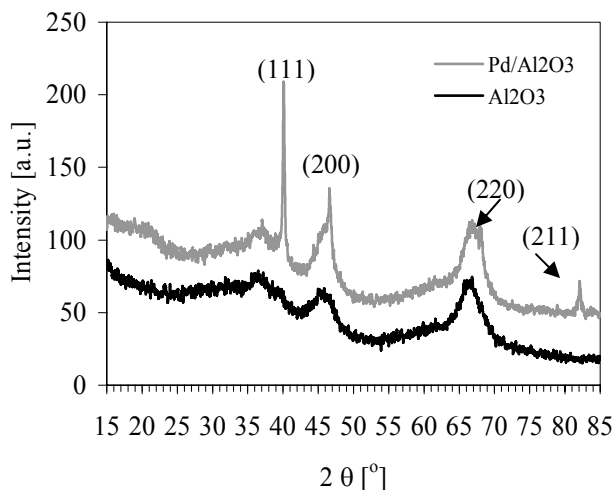


Fig. 3 – X ray powder diffraction pattern for  $\text{Pd}/\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ .

### NO temperature programmed desorption (NO – TPD)

NO – TPD measurements were performed in order to investigate the role of the catalytic surface in the adsorption and dissociation of NO on the

catalyst surface. Adsorption of NO on the catalyst surface is followed by desorption of NO,  $\text{N}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{O}_2$ , and small quantities of  $\text{NO}_2$ . This proves that formation of either reduced ( $\text{N}_2$ ,  $\text{N}_2\text{O}$ ) or oxidized species ( $\text{O}_2$ ,  $\text{NO}_2$ ) is possible on the catalyst surface<sup>10</sup> after NO chemisorption. Under reaction

conditions, in the presence of hydrogen as the reducing agent, only the reduced species N<sub>2</sub>, N<sub>2</sub>O were evidenced, because the chemisorbed O atoms are desorbed like H<sub>2</sub>O. For this reason, only desorption profiles of NO and of the reduced species (N<sub>2</sub>, N<sub>2</sub>O) are further presented and discussed.

Desorption profiles presented in the following (Fig. 4. (a)-(d)) suggest that NO is adsorbed on the catalyst molecularly as well as dissociatively, dissociated NO being further converted to N<sub>2</sub> and N<sub>2</sub>O. Dissociative adsorption of NO was previously reported for platinum group metal catalyst<sup>14,15</sup> or Cu/CeO<sub>2</sub>.<sup>16</sup>

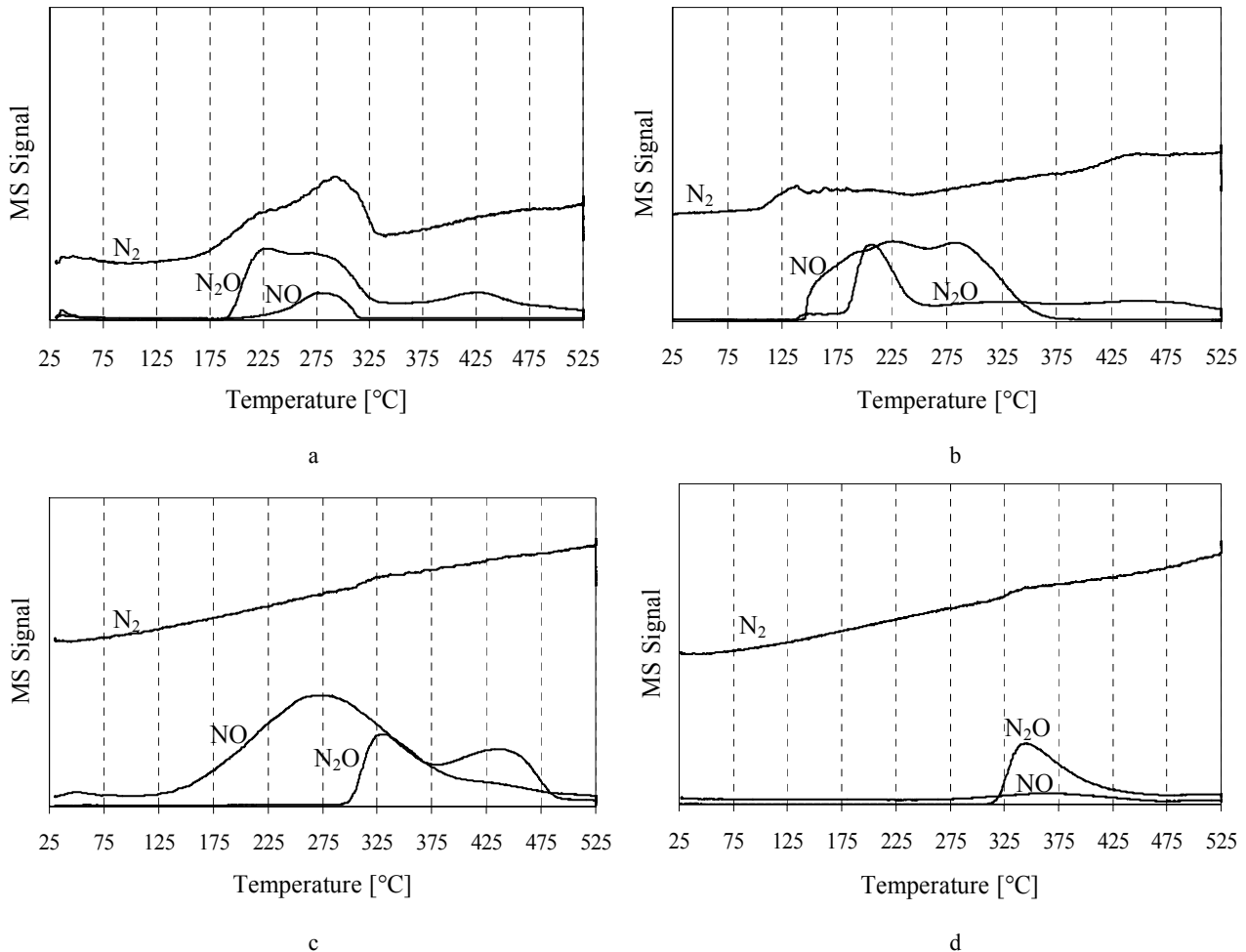


Fig. 4 – NO-TPD profiles (a) on Pd/Al<sub>2</sub>O<sub>3</sub>, NO adsorption at 25°C; (b) on Pd/Al<sub>2</sub>O<sub>3</sub>, NO adsorption at 150°C; (c) on Al<sub>2</sub>O<sub>3</sub>, NO adsorption at 25°C; (d) on Al<sub>2</sub>O<sub>3</sub>, NO adsorption at 150°C.

NO adsorption at 25°C occurs dissociatively more than molecularly resulting in larger amounts of N<sub>2</sub>O and N<sub>2</sub> that are desorbed from the catalyst (Fig. 4 (a)), compared to desorbed NO. NO, N<sub>2</sub>O and N<sub>2</sub> desorption profiles corresponding to the NO adsorption at 25°C are relatively similar as desorption peaks occur in the same temperature range: 180-325°C. Considering NO adsorption at 150°C, NO, N<sub>2</sub>O and N<sub>2</sub> desorption peaks are shifted towards lower temperatures. Desorption behaviours in this case are quite different. NO desorption profile is significantly larger (NO desorption temperature range between 150-350°C,

compared to 200-300°C for NO desorption corresponding to the adsorption at 25°C), three different desorption peaks being distinguishable. N<sub>2</sub>O desorption occurs in this case at 210°C compared to the first case in which N<sub>2</sub>O desorption occurred in a wider temperature range.

NO – TPD measurements were also performed on Al<sub>2</sub>O<sub>3</sub> without Pd loading in order to investigate the role of the support in the adsorption of NO. Results for NO – TPD on alumina revealed quite different desorption profiles compared to those corresponding to Pd loaded alumina. NO desorption curve corresponding to NO adsorption

on alumina at 25°C is significantly larger than that corresponding to Pd/Al<sub>2</sub>O<sub>3</sub> (desorption temperature range of 150-500°C – Fig. 4(c) compared to 200-300°C – Fig. 4(a)). Desorption peaks are broader and higher, while N<sub>2</sub>O and N<sub>2</sub> desorption peaks are quite negligible compared to those obtained for Pd/Al<sub>2</sub>O<sub>3</sub>. This suggests that NO adsorption at 25°C is strongly influenced by the presence of Pd particles on the catalyst. NO dissociates on the catalyst surface forming N<sub>2</sub>O, which at higher temperatures further dissociates to form N<sub>2</sub>.<sup>17</sup> Thus, at higher temperatures, N<sub>2</sub> desorption peak is greater than the desorption peak corresponding to N<sub>2</sub>O (Fig. 4 (a)).

NO desorption profile after NO adsorption on alumina at 150°C points out only a small but broad peak. In the case of Pd/Al<sub>2</sub>O<sub>3</sub> under same NO adsorption conditions (150°C) three larger peaks overlap one another. This reinforces the fact that Pd plays an important role regarding NO adsorption on the catalyst. These 3 peaks suggest that there are at least 2 different active sites which involve Pd: one might be metallic Pd, and the other one Pd-alumina interface.

Although NO – TPD on alumina showed that the support participates to a certain extent in the adsorption of NO, no significant N<sub>2</sub> formation was evidenced. This observation reinforces the conclusion that alumina does not influence the decomposition of N<sub>2</sub>O to form N<sub>2</sub>.<sup>18</sup>

## Catalytic activity results

Catalytic activity tests for H<sub>2</sub>-SCR of NO on Pd/Al<sub>2</sub>O<sub>3</sub> were performed at five temperature values in the range from 100 to 300°C at GHSV = 15,000 h<sup>-1</sup>, and NO:H<sub>2</sub> = 1:1.25. The reaction products of NO H<sub>2</sub>-SCR are N<sub>2</sub>, N<sub>2</sub>O and H<sub>2</sub>O. The obtained results prove that temperature strongly influences NO conversion, as well as the formation of reaction products.

For a working temperature of 100°C a maximum NO conversion of about 35 % is reached. Moreover, a significant amount of N<sub>2</sub>O was formed at this temperature. Working temperatures of 150°C and above led to total NO conversion, while the amount of produced N<sub>2</sub>O decreases with increasing temperature. Steady state is reached rapidly, in less than one hour, at each temperature.

The profiles of the effluent gases at 150°C are presented in Fig. 5. As soon as the reactant gases are passed over the studied catalyst, NO is readily transformed into products: N<sub>2</sub>, N<sub>2</sub>O and H<sub>2</sub>O. Total conversion of NO is to be noted at this temperature and above. Ammonia was not detected in the effluent gases at any of the investigated working temperatures. Nevertheless, no loss of catalytic activity was observed at any working temperature after 6 hours.

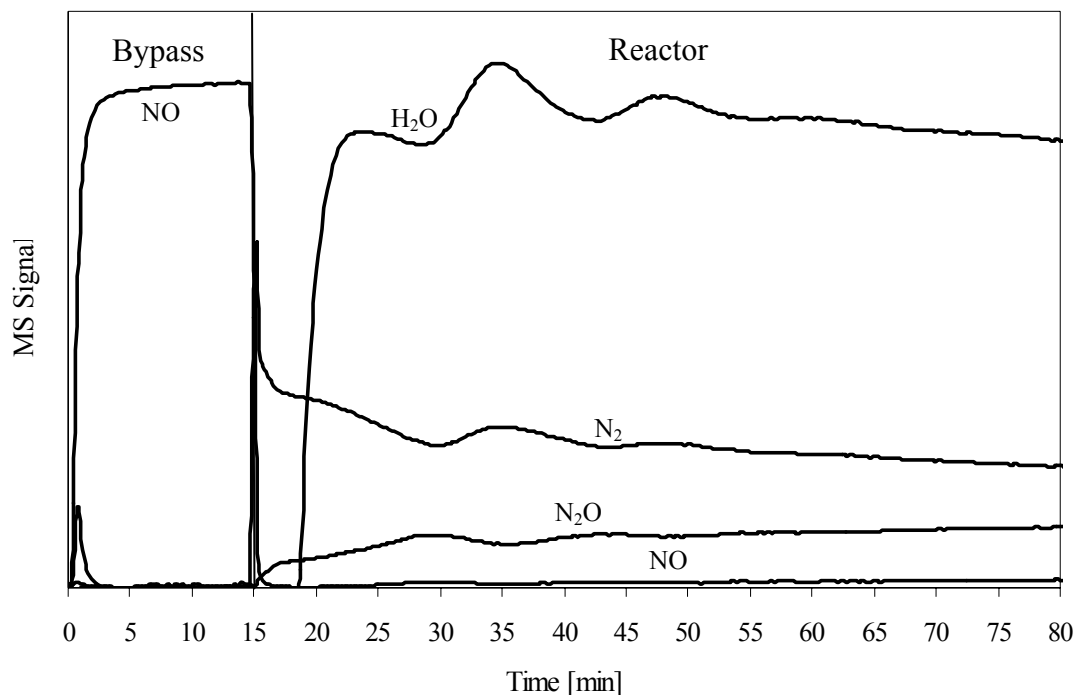


Fig. 5 – Profiles of the effluent gases for NO H<sub>2</sub>-SCR at 150°C, GHSV = 15,000 h<sup>-1</sup>, NO:H<sub>2</sub> = 1:1.25.

H<sub>2</sub>-SCR of NO was also investigated by increasing the reaction temperature from 50 to 350°C by a gradient of 5°C/min. NO conversion rises rapidly at temperatures up to 100°C, reaching 70% at this temperature. The difference between NO conversion at 100°C in this experiment and the one presented above is due to the different GHSV (lower GHSV values lead to increased values of NO conversion). Increasing the reaction temperature over 100°C results in a less rapid increase of NO conversion (see Fig. 6). Working temperatures above 150°C do not lead to higher NO conversion. Hydrogen conversion profile as a function of temperature is quite similar to that corresponding to NO.

At reaction temperatures bellow 110°C formation of N<sub>2</sub>O is more significant than that of N<sub>2</sub>. However, production of both N<sub>2</sub> and N<sub>2</sub>O is small due to low NO conversion. Above 110°C, N<sub>2</sub> selectivity increases in the detriment of N<sub>2</sub>O selectivity (see Fig. 7). No N<sub>2</sub>O is present in the effluent gases at temperatures above 175°C. Similar influence of temperature on the conversion of NO by reduction with hydrogen on PdMOR (Mordenite) or CePdMOR was reported by Pieterse and Booneveld<sup>3</sup>. Yu *et al.* reported as well that total NO<sub>x</sub> conversion is obtained on Pd/Al<sub>2</sub>O<sub>3</sub> or Pd/SiO<sub>2</sub> at temperatures above 200°C. However, formation of NH<sub>3</sub> was also reported for these catalysts.<sup>5</sup>

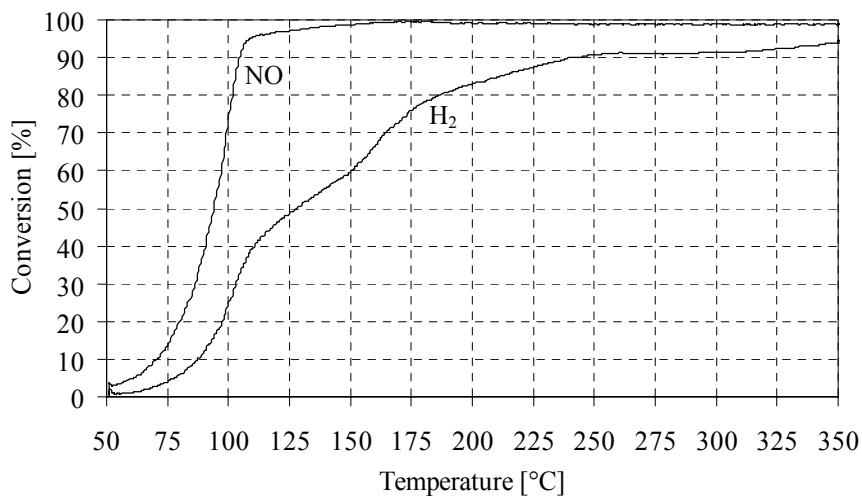


Fig. 6 – NO and H<sub>2</sub> conversion in H<sub>2</sub> – SCR on Pd/Al<sub>2</sub>O<sub>3</sub> as a function of temperature (reaction conditions: NO : H<sub>2</sub> = 1 : 1.10, GHSV = 7500 h<sup>-1</sup>).

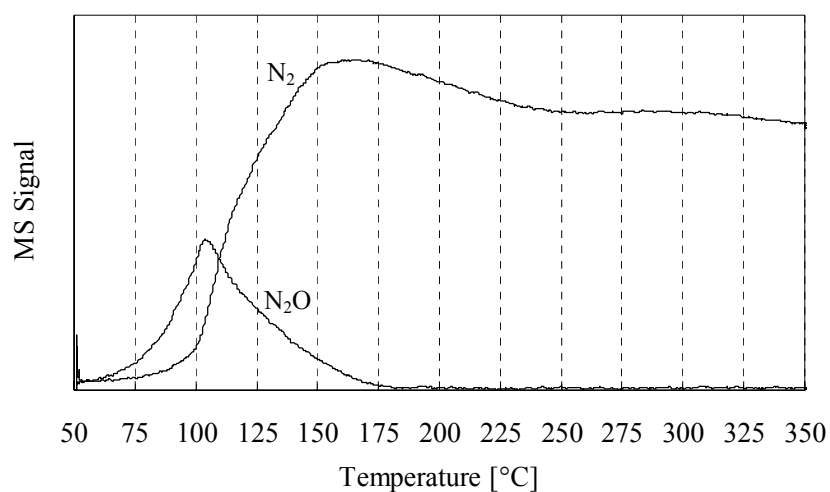


Fig. 7 – Influence of reaction temperature on the profiles of the reaction products (reaction conditions: NO : H<sub>2</sub> = 1 : 1.10, GHSV = 7500 h<sup>-1</sup>).

The catalytic activity results might be correlated with those obtained for NO – TPD. Thus, the low NO selectivity to N<sub>2</sub> at temperatures below 100°C is due to the dissociative adsorption of NO to form N<sub>2</sub>O. N<sub>2</sub>O is known to be reactive at higher temperatures leading to a higher NO selectivity to N<sub>2</sub> at temperatures above 150°C.

## EXPERIMENTAL

### Catalyst preparation

Catalyst preparation consisted in two steps. In the first step,  $\gamma$ -alumina was prepared by precipitation of an aqueous solution of Al(NO<sub>3</sub>)<sub>3</sub> with an aqueous solution of Na<sub>2</sub>CO<sub>3</sub> (1 M). The precipitate was kept at room temperature for 72 h, and then washed with distilled water for several times in order to remove the remaining Na<sup>+</sup> and NO<sub>3</sub><sup>-</sup> ions. After filtration, the precipitate was dried at room temperature for 24 h, and then at 105°C for another 24 h, followed by calcination at 400°C under Ar. The second preparation step consisted in the incipient wetness impregnation of the support with an aqueous Pd(NO<sub>3</sub>)<sub>2</sub> solution in order to obtain a metal loading of 1 wt. %. After impregnation, the catalyst was dried at 105°C for 8 h, calcined at 400°C under Ar, and finally reduced under H<sub>2</sub> at 400°C for 4 h.

### Catalyst characterization

Surface area (S<sub>p</sub>) and pore volume (V<sub>p</sub>) of the samples were measured by N<sub>2</sub> adsorption–desorption at -196°C using a Sorptomatic 1990 instrument (Thermo Electron). Each sample was degassed for 3 hours at 200°C prior to adsorption measurements.

X ray powder diffraction patterns were obtained using a Bruker D8 Advanced Diffractometer, working at 40 kV and 40 mA with CuK $\alpha$ 1 radiation, and a germanium monochromator. Measurements were performed in the angle range  $2\theta = 15 - 85^\circ$  and with a step-scanning mode of  $\Delta 2\theta = 0.01^\circ$ . Scherrer's equation was used to evaluate the dimension of the crystallites.

For NO temperature-programmed desorption (NO-TPD), 2 g of catalyst was placed in a fixed bed reactor (Microactivity Test Reactor, PID Eng&Tech), activated in pure H<sub>2</sub> at 300°C for 1 h, and then cooled in Ar to 25°C. The catalyst sample was further passed by a gas mixture of 2% NO in Ar for 30 min at adsorption temperatures of 25 and 150°C, and then purged by Ar in order to clean the catalyst of NO. A temperature programme of 5°C/min from 25 to 525°C was applied, while the effluent gases were analyzed by a mass spectrometer.

### Catalytic activity measurements

The activity tests were performed using a fixed bed reactor (Microactivity Test Reactor, PID Eng&Tech) at atmospheric pressure, working with varying NO:H<sub>2</sub> ratios and at reaction temperatures from 100 to 300°C. 1 g of catalyst was used for each test, corresponding to a GHSV of 15,000 h<sup>-1</sup>. Catalyst activation was performed before each measurement under H<sub>2</sub> at 300°C, for 1 h. The feed consisted in a mixture of NO in Ar (2 vol.% NO) and pure hydrogen which were supplied from independent mass flow controllers, and then mixed in a gas mixer. Continuous analysis of the effluent gases was achieved

by means of a quadrupole mass spectrometer, QMS, (PrismaPlus, Pfeiffer Vacuum) coupled to the reactor.

## CONCLUSIONS

The efficiency of hydrogen selective catalytic reduction of NO on a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst at temperatures below 300°C was investigated in this study. Both catalyst and reducing agent proved to be efficient at low temperatures. The reaction products of NO H<sub>2</sub>-SCR are N<sub>2</sub>, N<sub>2</sub>O and H<sub>2</sub>O. Temperature has a direct influence on NO conversion, but an increase of temperature over 150°C doesn't lead to important advantages regarding NO conversion. Total NO conversion at temperatures above 175°C was obtained at a reactant ratio NO:H<sub>2</sub> = 1:1.25, and GHSV = 15,000 h<sup>-1</sup>. Moreover, N<sub>2</sub>O formation as byproduct is also influenced by the reaction temperature. NO-TPD results indicate that N<sub>2</sub>O is formed as a consequence of NO dissociative adsorption on the catalyst surface, which further dissociates at higher temperatures in order to form N<sub>2</sub>. Thus, the largest amount of N<sub>2</sub>O is formed at temperatures below 120°C, while at temperatures above 175°C there is no evidence of N<sub>2</sub>O. Pd proved to play an important role in the adsorption of NO on the catalyst surface, and thus in the overall H<sub>2</sub>-SCR mechanism. At least 2 different active sites involving Pd were evidenced by the NO-TPD results, most probably metallic Pd and Pd-alumina interface. However, further investigations should be performed in order to determine the nature of these active sites, as well as to determine the influence of the amount of Pd on the efficiency of NO H<sub>2</sub>-SCR.

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