Desorption and catalytic properties of palladium, supported on Al_2O_3–La_2O_3, prepared by the sol–gel method

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Desorption and catalytic properties of 0.3 wt% Pd catalysts supported on alumina–lanthana, prepared by the sol–gel method, were studied. A large excess of consumed hydrogen was observed during TPR experiments on these catalysts due to the partial reduction of lanthana. The enhanced hydrogen adsorption (H/Pd varies from 8 to 15) detected by TPD for these catalysts is supposed to be a consequence of spillover. Spillover of hydrogen is favored by a high dispersion of palladium on the support surface and the presence of lanthana reduced species. Palladium on alumina–lanthana catalysts show a higher catalytic activity than palladium on alumina catalysts because reduced species of lanthana stabilize palladium particles. Similarity of ammonia selectivity at high temperatures allows one to suggest that reduced lanthana is involved in the reaction on pure alumina–lanthana support and palladium on alumina–lanthana catalysts at these temperatures. A synergetic effect between small palladium particles and reduced species of lanthana is suggested to be responsible for observed behavior of the lanthana-promoted palladium catalysts.

Keywords: Pd/Al_2O_3–La_2O_3 catalysts, NO reduction, hydrogen spillover, sol–gel preparation method

1. Introduction

Development of effective catalysts for NO_x abatement remains an important goal for pollution control in order to meet stringent regulations. More active and stable catalysts are required. On the other hand, because of the rapidly escalating price of expensive metals (for example rhodium), the industry needs the creation of lower-cost NO_x reduction catalysts. Palladium-only three-way catalysts are attractive for application in catalytic converters due to lower cost of palladium and their high-temperature durability [1]. These catalysts were found to be acceptable for commercial applications in automotive exhaust catalysts [2]. In order to improve activity or selectivity of palladium catalysts, closed-loop control systems are used [3].

Another method of acceleration of the nitric oxide reduction on these catalysts is to use the basicity of a lanthana promoter. It was found that palladium catalysts promoted by lanthana have similar activity as Rh-containing catalysts in NO_x, CO and hydrocarbons removal from automotive exhaust gases under near-stoichiometric conditions [4].

Usually three-component Pd–lanthana–alumina catalysts are prepared by impregnation of Pd/Al_2O_3 with La_2O_3 [5,6]. In the present work, Al_2O_3–La_2O_3 supports were prepared by the sol–gel method. Subsequent addition of palladium was through impregnation with palladium salt solution.

The sol–gel method is effective for the preparation of thermostable supports [7]. Mizukami et al. used this technique for preparation of thermostable alumina mixed oxides for combustion catalysts [8]. They observed that addition of cations such as Ba^{2+}, La^{3+}, Sr^{2+} or Zr^{4+} improves the thermal stability of alumina. Application of the sol–gel method is expected to make the Al_2O_3–La_2O_3 support more homogeneous, and this could result in new adsorption and catalytic properties of supported metal catalysts on this basis. However, we could not find data devoted to the study of palladium, supported on alumina–lanthana, prepared by the sol–gel method, in the literature. Therefore, the aim of the present work is to study catalytic and desorption properties of Pd supported on alumina–lanthana, prepared by the sol–gel method.

2. Experimental

2.1. Sample preparation

Mixed lanthana–alumina supports with 5 wt% La (5.8% La_2O_3) were prepared by the sol–gel method using aluminum sec-butoxide $Al(O\text{-}SBu)_3$ and lanthanum acetylacetonate $La(acac)_3 \cdot 2H_2O$ as precursors. These reagents were dissolved in hexylene glycol and ethanol, respectively, in accordance with the method reported by Masuda et al. [9]. Aluminum–lanthanum hydroxide sol

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was heated up to 373 K, stirred up and maintained under these conditions for 3 h.

Gel was formed by water addition at 393 K. Then the gel was kept under these conditions for 10 h. It was dried under vacuum at 373 K for 10 h and treated in nitrogen flow at 523 K for 4 h and 723 K for 12 h. Some samples were calcined at 1273 K for 3 h in order to observe their resistance to sintering.

Alumina was prepared by the same sol–gel method as the alumina–lanthana support without procedure of lanthanum addition. Palladium (0.3 wt%) catalysts supported on alumina–lanthana were prepared by impregnation of Al_2O_3–La_2O_3 with palladium chloride at 313 K for 40 min. The impregnated support was filtered under vacuum and dried in an oven in nitrogen flow at 383 K for 12 h. Finally, the catalysts were calcined at 873 K for 3 h before reduction. Reduction of the catalysts was carried out during hydrogen pretreatment before TPD experiments and catalytic reaction.

Pd/Al_2O_3 catalysts (with 0.3, 1 and 2 wt% Pd) were prepared by impregnation of Al_2O_3 (Rhone Poulenc, surface area 204 m^2/g) with Pd acetylacetonate solution. These samples were dried at 353–373 K overnight and reduced by hydrogen at 673 K for 4 h.

2.2. Characterization

Surface area measurements were carried out by low-temperature nitrogen adsorption in a volumetric equipment Gemini 2600 from Micromeritics. Calculations were performed on the base of the BET isotherm.

Temperature-programmed desorption (TPD) and reduction (TPR) spectra of hydrogen were measured using a thermodesorption apparatus AMI-M, Altamira Instruments. Before hydrogen adsorption the samples were pretreated with hydrogen at 673 K for 1, 2 or 3 h. Hydrogen adsorption was carried out at room temperature for 10 min. After sample flush in argon flow at room temperature, desorption spectra were registered during temperature increase with rate 20 K/min. Ultrahigh purity (minimum 99.999%) hydrogen and argon were used (100 and 10% H_2 in argon for TPD and TPR experiments, respectively). Deconvolution of two unresolved peaks was made with the standard procedure included in the software program of the AMI-1 unit. This procedure presents splitting of two unresolved peaks with vertical line dropped to baseline.

Reduction of NO by hydrogen in the range 323–973 K was studied in a continuous-flow microreactor

Table 1
Surface areas for Al_2O_3 and Al_2O_3–La_2O_3 samples after different temperature treatments

Sample	Treatment type	Temperature (K)	Duration (h)	Surface area (m^2/g)	Average surface area (m^2/g)
Al_2O_3-1	A	523 723	3 4	270	270
Al_2O_3-2	A	523 723	3 4	270	
Al_2O_3-3	B	523 723	4 12	318	–
Al_2O_3–La_2O_3-6	B	523 723	4 12	315	313
Al_2O_3–La_2O_3-8	B	523 723	4 12	312	
Al_2O_3–La_2O_3-10	B	523 723	4 12	312	
Al_2O_3-4	C	523 1273	4 3	118	–
Al_2O_3–La_2O_3-7	C	523 1273	4 3	134	127
Al_2O_3–La_2O_3-9	C	523 1273	4 3	115	
Al_2O_3–La_2O_3-11	C	523 1273	4 3	131	

Multipulse RIG 100, in situ research instrument under atmospheric pressure. Sample mass was 100 mg. Catalysts were pretreated before the catalytic measurements in hydrogen flow at 673 K for 1 h. The concentration of the reaction mixture in helium was 5% with an NO/H_2 molar ratio equal to 0.5. The flow rate of reaction mixture was 120 cm^3/min (at room temperature and under atmospheric pressure). Samples were kept for 40 min at each temperature and 10 min were needed to reach the next temperature. As a result of the catalytic reaction oxygen from NO is included into N_2O and water product molecules. Analysis of hydrogen and water was not performed on the experimental unit.

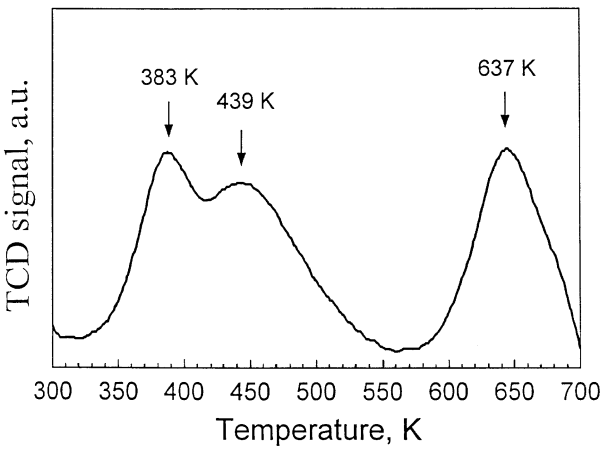

Figure 1. TPR spectrum of 0.3% Pd/Al_2O_3–La_2O_3.

3. Results

3.1. Surface area

As shown in table 1, during preparation of alumina and alumina–lanthana supports different thermal procedures were carried out. Thermal treatments were realized in two steps: a low-temperature step, common for all treatments, at 523 K for 3 or 4 h in flowing nitrogen and a high-temperature step either at 723 K for 4 or 12 h in flowing nitrogen (treatments A and B, respectively) or at 1273 K for 3 h in air atmosphere (treatment C). Surface areas were determined after these treatments.

Results, presented in table 1, allowed us to choose alumina–lanthana, prepared by treatment B, as supports for palladium catalysts preparation, because this treatment yields supports with maximum surface areas (around 300 $m^2\,g^{-1}$).

3.2. Temperature-programmed methods

3.2.1. TPR

Experimental results of hydrogen consumption during the reduction of the 0.3 wt% Pd/Al_2O_3–La_2O_3 catalyst are shown in figure 1. The TPR spectrum exhibits three peaks at 383, 439, and 637 K. According to calculations, hydrogen uptakes of 14.3, 19.5 and 29.2 μmol/g of catalyst correspond to these peaks, respectively. The value of total hydrogen consumption during TPR experiments exceeds that necessary for conversion of PdO into metallic palladium by a factor of 2.2.

3.2.2. TPD

The results of hydrogen desorption from Pd/Al_2O_3–La_2O_3 catalysts as a function of hydrogen pretreatment are illustrated in figure 2. The TPD spectra of Al_2O_3 and Al_2O_3–La_2O_3 supports are depicted in the same figure. The desorption peaks for the Pd catalysts appear in the temperature range 380–540 K and their broadening depends on the pretreatment time. Peaks become increasingly narrow as the pretreatment time increases from 1 to 3 h, and as a result the average amount of desorbed hydrogen decreases (table 2). The peaks of hydrogen, desorbed from Al_2O_3 and Al_2O_3–La_2O_3 supports, appear at temperatures higher than 523 K. The H/Pd ratios, calculated from the amount of hydrogen desorbed from Pd/Al_2O_3–La_2O_3 catalysts, are also shown in table 2. For these calculations the amount of hydrogen desorbed from the support was subtracted.

Another set of TPD experiments was conducted to investigate the effect of gas atmosphere between measurements. These results are presented in figure 3. The catalysts, previously pretreated for 2 h in hydrogen at

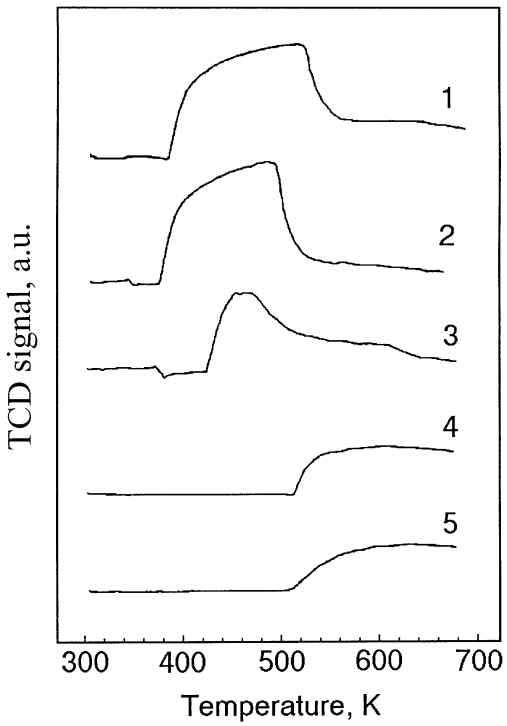

Figure 2. TPD spectra of 0.3% Pd/Al_2O_3–La_2O_3 after pretreatment in hydrogen for (1) 1 h, (2) 2 h and (3) 3 h; (4) Al_2O_3–La_2O_3 for 2 h, and (5) Al_2O_3 for 2 h.

Table 2
TPD results for Al_2O_3–La_2O_3 and Pd/Al_2O_3–La_2O_3 samples

Sample	Reduction time (h)	Average amount of desorbed H_2 (μmol/g sample)		H/Pd (%)
		without support correction	with support correction [a]	
Al_2O_3	2	84	–	–
Al_2O_3–La_2O_3	2	84	–	–
Pd/Al_2O_3–La_2O_3	1	295	211	15.0
Pd/Al_2O_3–La_2O_3	2	203	119	8.4
Pd/Al_2O_3–La_2O_3	3	197	113	8.0

[a] Subtraction of hydrogen adsorption of the support was made.

673 K, were characterized again after sample storage in air for six months. The amount of desorbed hydrogen enhanced after this storage. However, the subsequent repetitions of this experiment, made without exposing the sample to air, show only small peaks very similar to those observed for the support.

These results indicate that hydrogen pretreatment duration as well as the conditions of sample storage between subsequent TPD measurements have significant influence on hydrogen adsorption properties of Pd/Al_2O_3–La_2O_3 catalysts.

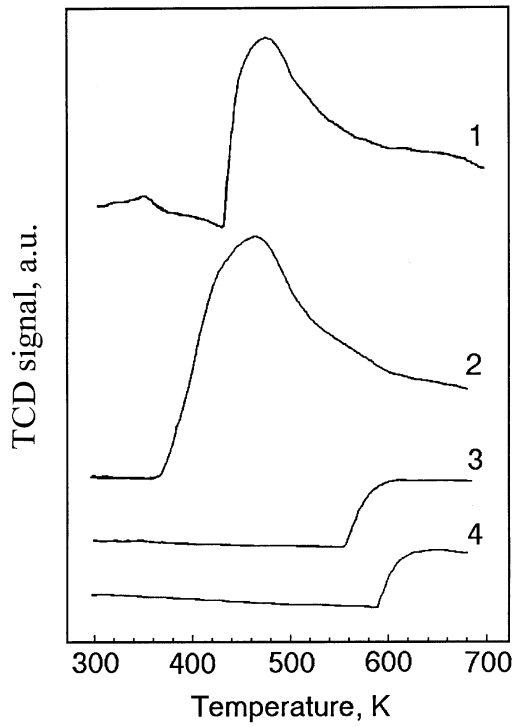

Figure 3. TPD spectra of 0.3% Pd/Al_2O_3–La_2O_3: (1) fresh sample portion (experiment No. I); (2) repetition of experiment No. I with the same sample portion after sample storage in air for 6 months (experiment No. II); (3) after experiment No. II and sample storage overnight in Ar at room temperature (experiment No. III); (4) after experiment No. III and sample storage overnight in Ar at room temperature (experiment No. IV).

3.3. Reaction of NO with hydrogen

Typical plots of NO conversion vs. temperature for all palladium catalysts are shown in figure 4. Palladium on alumina catalysts show a similar activity pattern which is independent of palladium concentration (0.3, 1.0, and 2.0 wt%). For these catalysts, NO conversion first increases with temperature, then decreases before passing through a minimum. The Pd/Al_2O_3–La_2O_3 catalyst behaves differently when temperature increases in that it exhibits no inflection of the NO conversion at any temperature. By this reason, Pd/Al_2O_3–La_2O_3 catalysts show higher catalytic activity than all Pd/Al_2O_3 catalysts in the range 473–573 K.

As far as selectivity is concerned, the observed products of the reaction were N_2O, N_2, and NH_3 (figure 4). The N_2O concentration is maximum at 423 K for all catalysts, then it becomes equal to zero at 523 and 673 K for Pd/Al_2O_3–La_2O_3 and Pd/Al_2O_3 catalysts, respectively.

For nitrogen concentration, a maximum was observed in the interval 423–523 K for all catalysts. At higher temperatures for the Pd/Al_2O_3–La_2O_3 catalyst, nitrogen concentration remains constant. In contrast, for all Pd/Al_2O_3 catalysts nitrogen concentration increases sharply with temperature.

For ammonia concentration the difference between lanthana-promoted and non-promoted catalysts is also very pronounced. The Pd/Al_2O_3–La_2O_3 catalyst yields 80% ammonia concentration while Pd/Al_2O_3 catalysts yield less than 50%.

The results of catalytic experiments with Al_2O_3–La_2O_3 support are illustrated in figure 5 . At temperatures lower than 673 K activity of the support was very small. At temperatures higher than 673 K moderate activity with predominant ammonia formation was detected. Ammonia selectivity is about 80%. Hence, ammonia selectivity of Al_2O_3–La_2O_3 is similar to that of Pd/Al_2O_3–La_2O_3 catalysts at high temperatures.

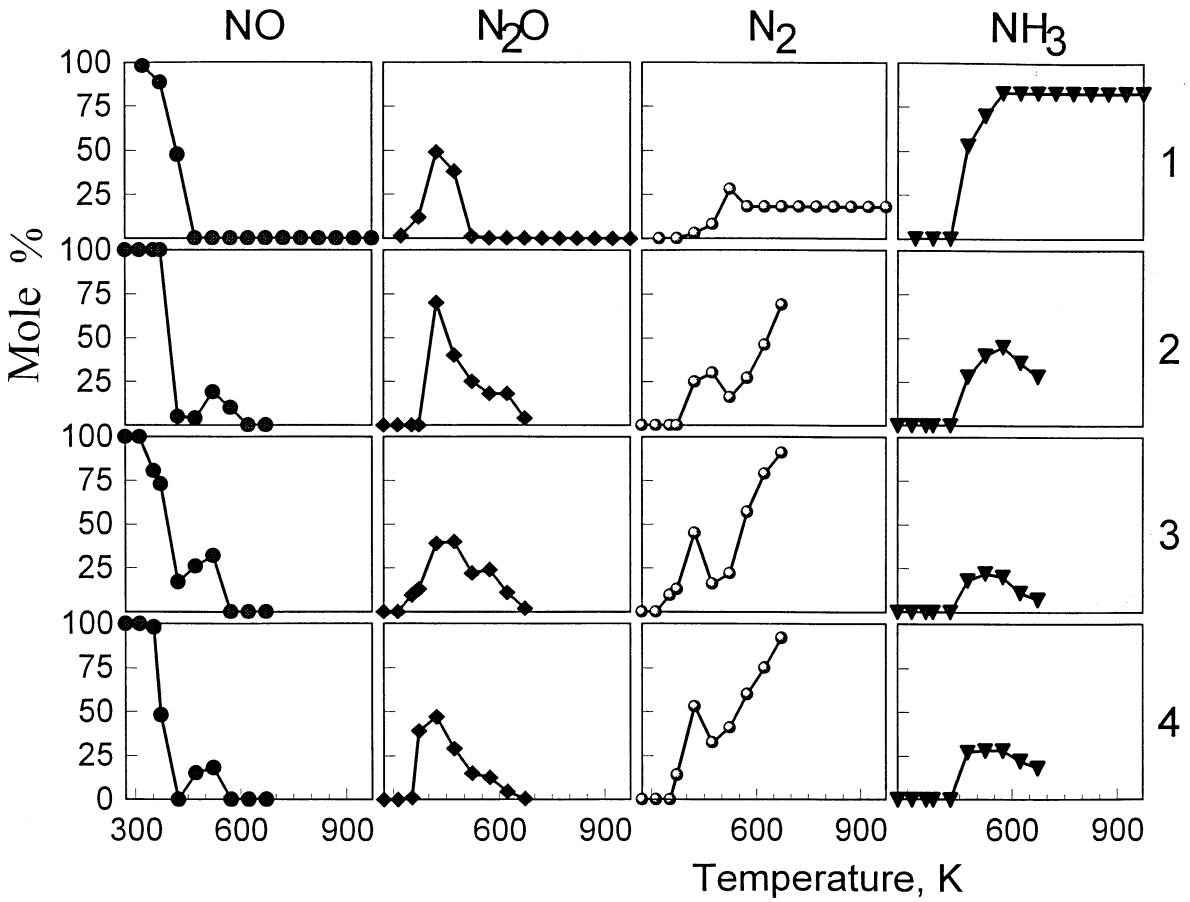

Figure 4. NO conversion and product distributions as function of reaction temperature for: (1) 0.3% Pd/Al_2O_3–La_2O_3; (2) 0.3% Pd/Al_2O_3; (3) 1% Pd/Al_2O_3; and (4) 2% Pd/Al_2O_3.

4. Discussion

4.1. Surface area

Different types of treatment resulted in variation of surface area of supports. The average surface area of alumina supports after treatment A was found to be equal to 270 m^2/g (table 1). Increase of treatment time at 723 K from 4 to 12 h leads to a $\sim$ 180% increase of specific surface area to 318 m^2/g, indicating that long time is required to reach the final microporous structure of alumina, prepared by the sol–gel method. A temperature increase from 723 to 1273 K results in 63% decrease of alumina surface, presumably due to sintering.

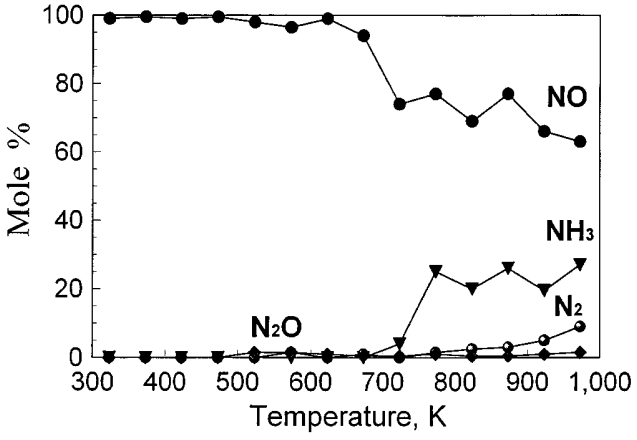

Figure 5. NO conversion and product distributions as a function of reaction temperature for Al_2O_3–La_2O_3.

Addition of lanthana to alumina during sol–gel preparation did not change significantly (318 and 313 m^2/g) its surface area after treatment B. However, it increases slightly (from 118 to 127 m^2/g) the support surface area after treatment C. These data are in agreement with those reported by Subramanian et al. [10] who observed that the surface area of lanthana–alumina composite oxides does not change while lanthana concentration increases up to 8.0 wt%, but decreases for higher concentrations. In the present work the lanthana loading (5.8 wt%) is lower than the saturation value of 8 wt% reported in ref. [10], and therefore the effect of lanthana on the surface area value is not observed. These results also agree with those reported in ref. [8], where 10 wt% lanthana–alumina samples, prepared by the sol–gel method and calcined at 1273 K for 3 h, showed surface areas ranging from 85 to 171 m^2/g.

Table 3
Surface area of samples before and after TPD of hydrogen

Sample	Duration of hydrogen pretreatment for TPD (h)	Surface area (m^2/g sample)		Surface are decrease after TPD (%)
		before TPD	after TPD	
Al_2O_3–La_2O_3	2	313	304	3.1
Pd/Al_2O_3–La_2O_3	1	265	251	5.3
Pd/Al_2O_3–La_2O_3	3	265	251	5.3

After impregnation of the Al_2O_3–La_2O_3 support with an aqueous solution of palladium chloride and calcination at 873 K for 3 h, a 15% decrease of the surface area was observed (table 3). This is due to increase of final treatment temperature from 723 (for support) to 873 K (for Pd/Al_2O_3–La_2O_3). After the TPD experiments the surface area of support and catalysts were reduced very little (3 and 5%, respectively). When duration of hydrogen pretreatment before TPD experiments increased from 1 to 3 h, a measurable variation of surface area was not observed (table 3). These results can be explained by the fact that the temperature during TPD experiments was lower than during the sample preparation.

4.2. Temperature-programmed reduction

The TPR spectra of calcined catalyst exhibit three peaks at 383, 439 and 637 K (figure 1). The peaks at 383 and 439 K may be attributed to the two-step reduction of palladium oxide because in this temperature range (at 423 [11] or 437 K [12]) TPR spectra of Pd/alumina catalysts show peaks assigned to reduction of palladium oxide.

Additional evidence for such explanation can arise from the integrated hydrogen consumption (figure 1). Calculations showed that the combination of both peaks corresponds quite well with the hydrogen amount needed for the reduction of palladium oxide (PdO) to metallic palladium. The first peak can be due to the partial reduction of PdO to Pd_2O:

$$2PdO + H_2 \rightleftharpoons Pd_2O + H_2O$$

while the second corresponds to the reduction of Pd_2O to metallic Pd:

$$Pd_2O + H_2 \rightleftharpoons 2Pd + H_2O$$

Hydrogen volumes, calculated from first and second peaks, corresponded to 102 and 138% of those necessary for first and second reactions, respectively.

The third peak at 637 K may be related with the reduction of lanthana. Although reduction of pure La_2O_3 did not occur in the temperature interval from room temperature to 650 K [5] or 973 K [13], the peak at 433–440 K for Pd/La_2O_3 was ascribed to partial reduction of La_2O_3 in the vicinity of Pd [5]. In our case for Pd/Al_2O_3–La_2O_3 catalysts this peak is shifted by 200 K to higher temperature as compared with ref. [5], probably because of strong interaction of La_2O_3 with Al_2O_3 in Al_2O_3–La_2O_3 support prepared by the sol–gel method. Assuming the following equation for lanthana reduction:

$$La_2O_3 + H_2 \rightleftharpoons 2LaO + H_2O$$

about 16% La_2O_3 was reduced according to the third TPR peak. Significant lanthana reduction can be attributed to the existence of a good intimate contact between Pd and lanthana provided by the preparation method.

Considering these three peaks, a 120% excess of hydrogen consumption over the amount necessary for complete PdO reduction was measured in the present work. Excess of H_2 uptake was also reported for other Pd- and La-containing samples supported on oxides. For example, lanthana was supported on Pd/SiO_2 and 6% of hydrogen consumption excess was registered [5,6]. Excess hydrogen uptake in the range 8–29% was registered for Pd–La/zeolite-X (1.78% Pd) samples compared with Pd/zeolite-X alone [14].

4.3. Temperature-programmed desorption

Spectra of hydrogen desorption from Al_2O_3 and Al_2O_3–La_2O_3 supports are very similar (figure 2). Desorption initiates at 510 K and does not complete in the investigated temperature range ($\leqslant$673 K). These data agree with those of Vaarkamp et al. [15], where hydrogen desorption from Al_2O_3 began at $\sim$ 553 K and did not finish until 873 K.

For lanthana-promoted samples H/Pd ratios vary from 8 to 15, depending on the duration of hydrogen pretreatment (table 2). These results suggest that spillover takes place. Spillover of hydrogen is often observed on supported metals, yielding hydrogen/metal ratios as high as 5.6 [16]. For alumina, prepared by the sol–gel method, hydrogen spillover from small palladium particles was reported [17]. H/Pd ratios obtained in this work are considerably higher than the typical values observed for alumina during spillover. This is apparently due to the formation of additional adsorption sites by the reduction of lanthana. Adsorption on the support may occur when the support is easily reduced by hydrogen as in the case of lanthana, titania [8], or ceria [12].

It should be mentioned that considerable hydrogen uptakes (H/Pd = 12) were recently observed for a lanthanide-promoted catalyst (Yb–Pd/SiO_2) in the hydrogenation of propene [19]. Part of observed high

hydrogen uptakes is apparently due to the formation of additional adsorption sites by the reduction of lanthana. Thus, enhanced hydrogen adsorption ($8 \leqslant H/Pd \leqslant 15$) detected by TPD is assigned to hydrogen spillover from well dispersed palladium particles to alumina and reduced lanthana. Absorption of hydrogen was excluded from consideration due to the data of Boudart and Hwang. They showed that the H/Pd ratio is near 0.2 for hydrogen absorption at room temperature under atmospheric pressure for small palladium particles ($D > 50\%$) [20]. Palladium particles in 0.3% Pd/Al_2O_3–La_2O_3 are suggested to be small because of low metal concentration, high surface area of support, and significant H/Pd ratios observed. This H/Pd ratio for hydrogen absorption is negligible as compared to observed ratios, which varied from 8 to 15.

A further insight into the phenomenon of hydrogen adsorption on the support may be given by experiments showing that storage conditions of the catalysts influence significantly the amount of hydrogen desorbed from Pd/Al_2O_3–La_2O_3 catalysts. It was observed that hydrogen uptake increased by a factor of two after storage in air for several months and decreased by a factor of four during consecutive experiments and storage in inert atmosphere. Such results show that adsorption sites were formed or eliminated with ease. According to the spillover mechanism, it is assumed that spillover is a function of the amount of hydroxyl groups [21,22], which, in turn, is a function of heating and storage conditions. Sample heating at high temperatures for a long time decreases surface hydroxylation. Storage in air (but not in inert gases) causes its rehydroxylation.

4.4. Catalytic reaction

Pd/Al_2O_3–La_2O_3 catalysts reach total conversion of NO at temperatures 150 K lower than Pd/Al_2O_3 catalysts. Moreover, Pd/Al_2O_3–La_2O_3 catalysts yield ammonia as the main product of the reaction at high temperatures. Hence, lanthana promotion of alumina makes palladium catalysts more active with a high selectivity to ammonia.

The phenomenon of activity drop with temperature registered for all studied Pd/Al_2O_3 catalysts is similar to that observed for palladium, both on silica and alumina catalysts, for the reduction of NO by CO [23]. According with the interpretation given in ref. [23], the activity drop is related with the relative facility of palladium to be oxidized in presence of oxidative atmospheres as a function of the temperature. The same scheme can be applied for results of this work.

On Pd/Al_2O_3–La_2O_3 catalyst, NO conversion is not accompanied by any activity drop with temperature. It can be suggested that reduction of lanthana in intimate contact with well dispersed palladium is responsible for this behavior.

On Pd/Al_2O_3–La_2O_3 catalyst, a constant 80% ammonia selectivity was observed at temperatures higher than 573 K. This ammonia yield is found to be limited by the molar H_2/NO ratio in the feed which was 2 instead of 2.5 (stoichiometric for 100% ammonia selectivity).

Results on lanthana–alumina support without palladium showed that at high temperatures (> 673 K) conversion of NO occurs with predominant formation of ammonia (figure 5). The temperatures of initiation of the reaction and reduction of lanthana essentially coincide (550 K, figures 1 and 5). An agreement also exists between temperatures of the end of sample reduction (700 K, figure 1) and maximum of ammonia production (773 K, figure 5). These data suggest that reduced sites of lanthana are able to reduce NO in the presence of hydrogen.

On the basis of results obtained for pure Al_2O_3–La_2O_3 support it is believed that the addition of palladium to lanthana–alumina phase, prepared by the sol–gel method, facilitates the occurrence of reduction of lanthana which in its turn favors the ammonia production. After palladium addition, the temperature of the reaction initiation is about 300 K lower than that on Al_2O_3–La_2O_3 support.

Hence, at low temperatures, Pd/Al_2O_3–La_2O_3 catalysts behave similar to Pd/Al_2O_3 catalysts. At intermediate temperatures, transformation of palladium particles occurs in Pd/Al_2O_3 catalysts accompanied by an activity drop. However, in Pd/Al_2O_3–La_2O_3 catalysts, formation and consequent inclusion in catalytic process of reduced lanthana sites prevents this transformation. At high temperatures, ammonia selectivity is very high for Al_2O_3–La_2O_3 support and Pd/Al_2O_3–La_2O_3 catalysts, indicating that addition of palladium to Al_2O_3–La_2O_3 results in keeping of the reaction path on reduced lanthana sites. At the same time, higher NO conversion on Pd/Al_2O_3–La_2O_3 catalysts compared to Al_2O_3–La_2O_3 gives evidence of enhancement of the concentration of these centers after palladium supporting due to hydrogen spillover.

A synergetic effect between palladium particles which carry out spillover and lanthana reduced species which increase hydrogen adsorption is suggested to occur in Pd/Al_2O_3–La_2O_3 catalysts. In the presence of hydrogen, small palladium particles promote the reduction of lanthana, forming active sites for NO reduction. Investigation of the catalysts by physical–chemical methods is necessary for deeper understanding of the observed effects. This investigation is now in progress, and the results will be published soon.

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