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Structural and catalytic properties of Pd/Al_2O_3–La_2O_3 catalysts

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Abstract

A new Pd/Al_2O_3–La_2O_3 catalyst has been synthesized for the reduction of NO with hydrogen. This catalyst is more active than coprecipitated Pd/Al_2O_3 catalysts. The revealed effect of the improvement of the catalytic activity at medium temperature and the increase of NH_3 formation at high temperatures for Pd catalyst supported on alumina–lanthana prepared by the sol–gel method are ascribed to a new lanthanum-containing phase observed by X-ray powder diffraction and high resolution electron microscopy. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Pd/Al_2O_3–La_2O_3 catalysts; Sol–gel preparation method; Nitrogen oxide reduction; NH_3 production

1. Introduction

Palladium-only three-way catalysts are attractive for application in catalytic converters [1], due to low cost of palladium and their high temperature durability. Palladium on alumina–lanthana catalysts show enhanced NO_x reduction as compared to palladium on alumina [2]. In Ref. [2] three-component Pd–lanthana–alumina catalysts were prepared by impregnation of Pd/Al_2O_3 with La_2O_3. The aim of the present work is to study the catalytic, sorption and structural properties of Pd catalysts supported on Al_2O_3–La_2O_3, prepared by sol–gel method. Application of sol–gel method can lead to improvement of alumina–lanthana contact and as a result to variation of catalytic properties. In the present work, Al_2O_3–La_2O_3 supports prepared by coprecipitation are used as a reference. Comparison of catalytic and structural properties of Pd on the supports prepared by coprecipitation and sol–gel is made.

2. Experimental

Mixed lanthana–alumina supports with 5 wt% La (5.8% La_2O_3) were prepared by sol–gel and coprecipitation methods using aluminum sec-butoxide $Al(o\text{-}sbu)_3$ and lanthanum acetylacetonate $La(acac)_3\cdot 2H_2O$ as precursors.

For support preparation by sol–gel method, precursors were dissolved in hexylene glycol and ethanol, respectively, in accordance with the method reported by Masuda et al. [3]. Aluminum–lanthanum hydroxide sol 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.

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For support preparation by coprecipitation method, aluminum sec-butoxide was added to 2-butanol butoxide at room temperature in a molar solvent/alkoxide ratio 2.3. The solution was heated up to 363 K (with a heating rate of 3 K/min) and stirred at this temperature for half an hour. Then lanthanum acetylacetonate was added to the solution. Alkoxide solution was stirred at the same temperature for 1 h and then cooled to 348 K. For the coprecipitation, deionized water was added dropwise to the solution at this temperature. Water/alkoxide molar ratio of the final mixture was equal to 5.5. After storage at room temperature for 24 h, the coprecipitated sample was washed with deionized water and filtered under vacuum.

Final treatment of Al_2O_3–La_2O_3 supports prepared by either coprecipitation or sol–gel method was heating in N_2 flow at 523 K for 4 h and then at 723 K for 12 h.

Palladium (0.3 wt%) catalysts supported on Al_2O_3–La_2O_3 were prepared by support impregnation with palladium chloride at 313 K for 40 min. The impregnated supports were filtered under vacuum and dried in N_2 flow at 383 K for 12 h. Finally, the catalysts were calcined at 873 K for 3 h before reduction in catalytic reactor.

The preparation of palladium (0.3 wt%) catalyst supported on γ-Al_2O_3 is described in Ref. [4]. La_2O_3 was prepared by decomposition of $La_2O_2(CO_3)$ in air flow at 923 K.

Characterization of the samples by TPD, TPR, XRD, XPS, TEM and procedure of the catalytic experiments is described in Refs. [4,5].

3. Results

3.1. Temperature-programmed methods

3.1.1. TPR

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

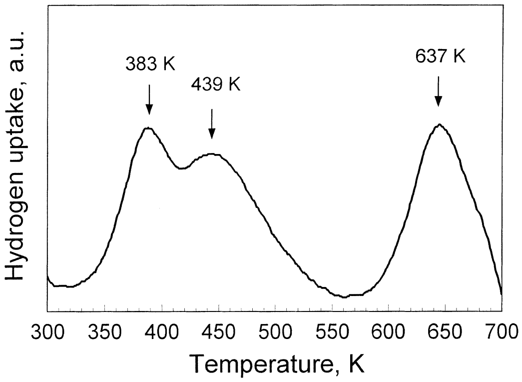

Fig. 1. TPR spectrum of sol–gel 0.3 % Pd/Al_2O_3–La_2O_3.

3.1.2. TPD

The H_2 desorption peaks for the 0.3 wt% Pd/Al_2O_3–La_2O_3 catalysts appear in the temperature range 380–540 K and they become increasingly narrow as the pretreatment time increases from 1 to 3 h, and as a result the average amount of desorbed H_2 decreases (Table 1). 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 1. For these calculations the amount of hydrogen desorbed from the support was subtracted.

3.2. Reaction of NO with hydrogen

3.2.1. Pd/Al_2O_3–La_2O_3 catalysts

NO conversion for sol–gel catalyst increases with temperature very sharply (Fig. 2). On catalyst prepared by coprecipitation, NO conversion is essentially lower than on the same catalyst prepared by sol–gel method. For that catalyst at the range 573–773 K, the slight decrease of NO conversion with temperature is observed in contrast to sol–gel catalyst (Fig. 2) and similar to Pd/Al_2O_3 catalysts (Fig. 3).

The observed products of the reaction are N_2O, N_2, and NH_3. The N_2O concentration is maximum (ca. 50 and 10 mol%) at 423 and 473 K then it becomes equal to zero at 523 and 673 K for samples prepared by sol–gel and coprecipitation, respectively. The temperature range of N_2O formation is 200 K for sol–gel catalyst and 300 K for coprecipitated catalyst and Pd/Al_2O_3 (Fig. 3). For N_2 concentration, a max-

Table 1
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–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.

imum was observed at 523 K for both samples. At higher temperatures, nitrogen concentration remains constant for the sample prepared by sol–gel method and goes through a minimum for the sample prepared by coprecipitation similar to Pd/Al_2O_3 catalysts (Fig. 3). Ammonia concentration increases with temperature more sharply in the case of sol–gel catalyst. The sol–gel catalyst yields 80% ammonia concentration at temperature higher than 573 K while coprecipitated one yields ca. 60% in the temperature range 573–773 K and then NH_3 concentration increases reaching ca. 80% at 973 K. A slightly pronounced maximum (less intensive than one on Pd/Al_2O_3 catalyst, Fig. 3) is observed on coprecipitated sample.

3.2.2. Al_2O_3–La_2O_3 supports

The results of catalytic experiments with Al_2O_3–La_2O_3 supports prepared by two methods are illustrated in Fig. 4. At temperatures lower than 673 and 873 K their activity was very small and at higher temperatures, moderate activity with predominant ammonia and nitrogen formation for sol–gel and coprecipitated supports, respectively, was detected. Very low nitrous oxide concentration (<2%) was observed only at temperature ≥873 K for both supports.

3.3. X-ray diffraction

The main peculiarity of X-ray diffractograms from La_2O_3-containing samples prepared by sol–gel method was the presence of a new crystalline phase, besides the peaks belonging to γ-Al_2O_3. The new phase was characterized by peaks at the following 2θ positions: 12.82; 25.16; 30.61; 33.82; 40.46; 43.82; 51.12 and 56.55° (Fig. 5a). In the diffractograms from La_2O_3-containing samples, prepared by coprecipita-

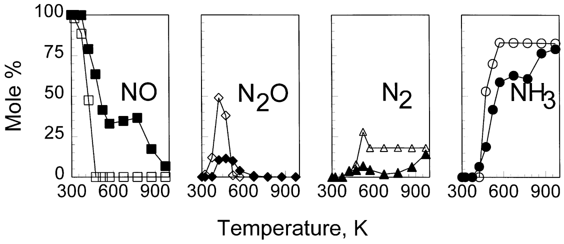

Fig. 2. NO conversion and product distributions as function of reaction temperature for 0.3% Pd/Al_2O_3–La_2O_3. White symbols — samples prepared by sol–gel method and black symbols — samples prepared by coprecipitation.

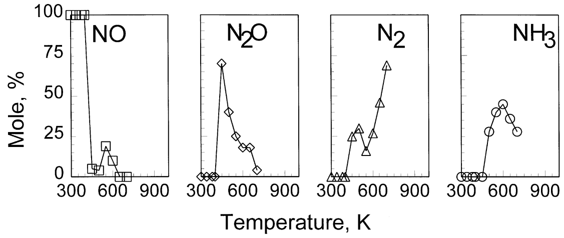

Fig. 3. NO conversion and product distributions as function of reaction temperature for 0.3% Pd/Al_2O_3.

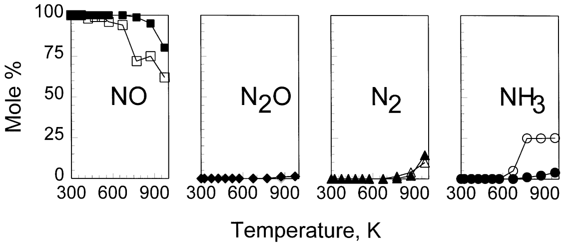

Fig. 4. NO conversion and product distributions as function of reaction temperature for Al_2O_3–La_2O_3. White symbols — samples prepared by sol–gel method and black symbols — samples prepared by coprecipitation.

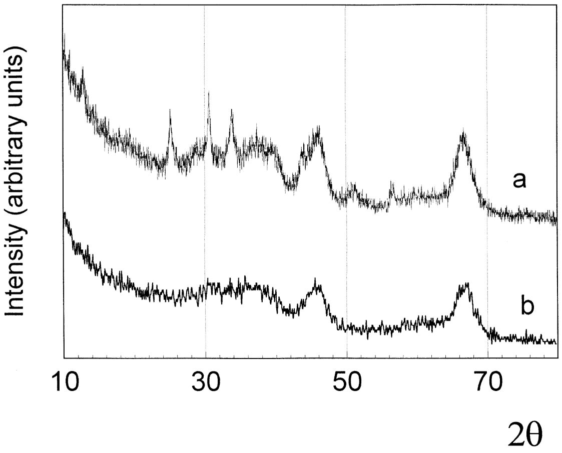

Fig. 5. X-ray diffractograms of sol–gel Al_2O_3–La_2O_3 (a) and coprecipitated Al_2O_3–La_2O_3 (b).

tion only peaks belonging to γ-Al_2O_3 were observed (Fig. 5b).

3.4. TEM

In sol–gel La_2O_3-containing samples, shapeless agglomerates, characterized by high contrast and looking like 'dark clouds', were observed (Fig. 6). These agglomerates were scarce, with sizes in the range 100–1000 nm and consisting of crystalline domains as shown in Fig. 7. In micrographs of Al_2O_3–La_2O_3, areas with high contrast ('dark clouds') are characterized by interplanar distances and angles between them as shown in Fig. 7. The interplanar distances measured in the magnified zones A, B and C are 0.334 and 0.326 nm with angle ∼72°; 0.296 and 0.262 nm with angle ∼85°; 0.331 and 0.295 nm with angle ∼79°, respectively. Palladium particles were not seen in images of the samples, in spite of great efforts to look for them on several zones of the catalyst. This suggests that dispersion of palladium is very high due to either the preparation conditions and/or low palladium concentration. In micrographs of coprecipitated Al_2O_3–La_2O_3 support, the 'dark clouds' were not noticed.

3.5. XPS

Results of XPS study are presented in Table 2. Pd $3d_{5/2}$ binding energy was found to be 336.2 eV for 0.3% Pd/Al_2O_3–La_2O_3. For almost all Al_2O_3–La_2O_3 containing samples, binding energy of La $3d_{5/2}$ peak was 836.2 eV. The spectra of dried Al_2O_3–La_2O_3 presented a shoulder at 834.6 eV next to the main peak of La $3d_{5/2}$ (836.5 eV). Binding energy of La $3d_{5/2}$ for La_2O_3 and Al_2O_3–La_2O_3 calcined at 1273 K was 835.1 and 835.7 eV, respectively.

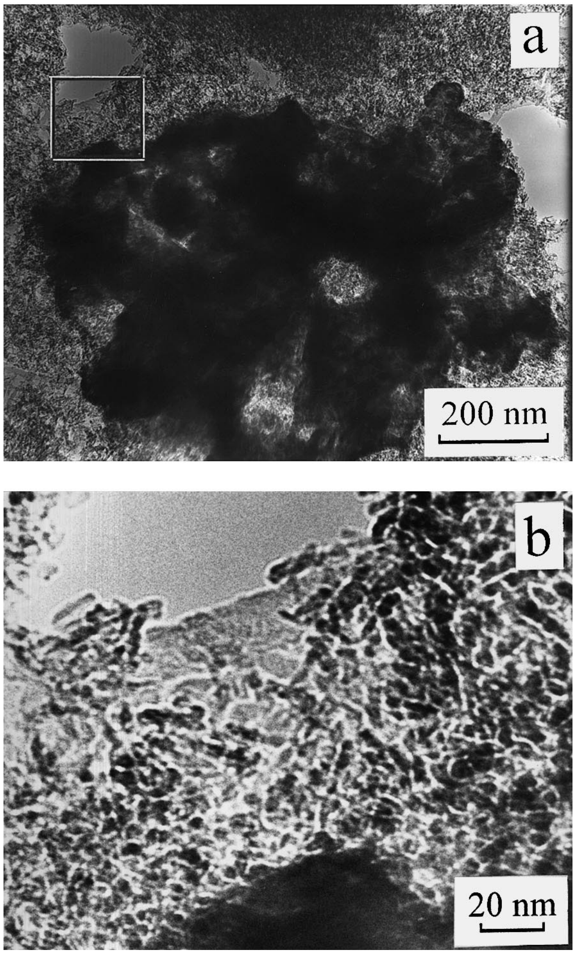

Fig. 6. TEM micrographs of general views of Al_2O_3–La_2O_3: area marked in (a) is magnified and represented as (b).

4. Discussion

4.1. Temperature programmed reduction

The TPR spectra of calcined catalyst exhibit three peaks at 383, 439 and 637 K (Fig. 1). The peaks at 383

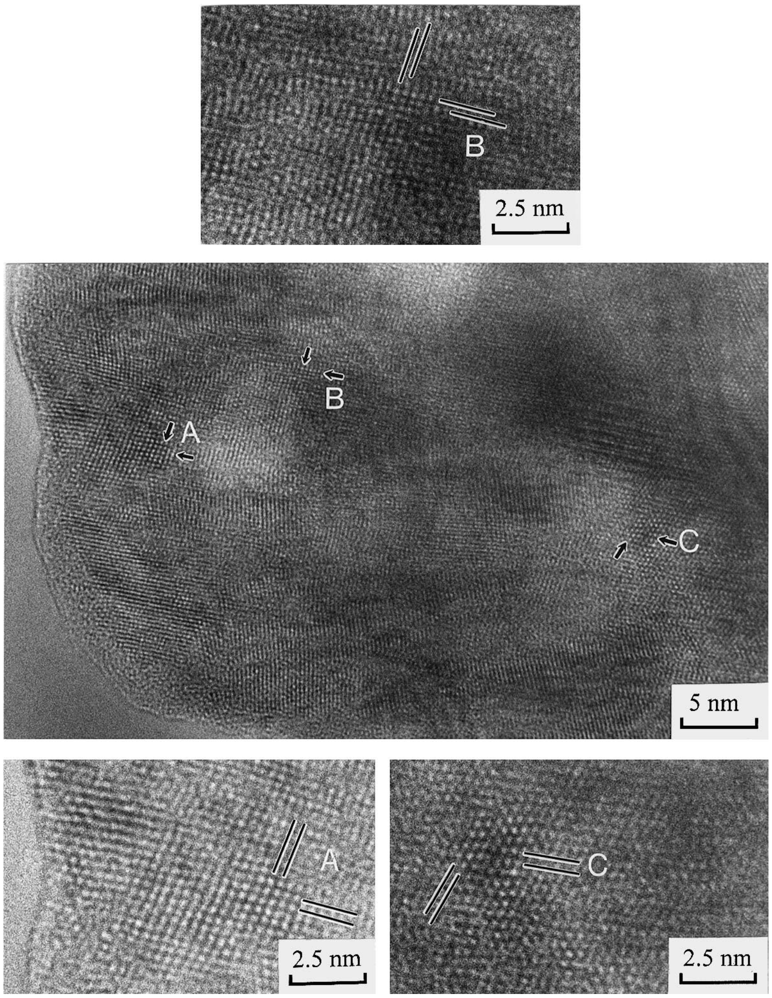

Fig. 7. HRTEM micrograph of La_2O_3–Al_2O_3. A, B and C are magnified zones, characterized by interplanar distances 0.334 and 0.326 nm with angle ∼72°; 0.296 and 0.262 nm with angle ∼85°; 0.331 and 0.295 nm with angle ∼79°, respectively.

and 439 K may be attributed to the two-step reduction of palladium oxide because in this temperature range (at 423 [6] or 437 K [7]) TPR spectra of Pd/alumina catalysts show peaks assigned to reduction of palladium oxide.

Hydrogen volumes, calculated from 1st and 2nd peaks, corresponded to 102 and 138% of those necessary for reduction of PdO to Pd_2O and Pd_2O to Pd, 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 [8] or 973 K [9], 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 [8]. In our case for Pd/Al_2O_3–La_2O_3 catalysts, this peak is shifted by 200 K to higher temperature by comparison with [8] probably because of strong interaction of La_2O_3 with Al_2O_3 in Al_2O_3–La_2O_3 support prepared by sol–gel method. Significant lanthana reduction can be attributed to the existence of a good intimate contact between Pd and lanthana provided by 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

Table 2
Elemental binding energies (eV) of studied samples

Sample	O1 s	Al 2p	La $3d_{5/2}$	Pd $3d_{5/2}$
La_2O_3	531.7 529.7 (shoulder)	–	835.1	–
Al_2O_3–La_2O_3 dried	531.7	74.4	836.5 834.6 (shoulder)	–
Al_2O_3–La_2O_3, calcined at 1273 K	531.3	74.3	835.7	–
Al_2O_3–La_2O_3 (reduced)	531.3	74.0	836.2	–
0.3% Pd/Al_2O_3–La_2O_3 (reduced)	531.2	74.0	836.2	336.2

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 [8,10]. 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 [11].

4.2. Temperature programmed desorption

For lanthana-promoted samples H/Pd ratios vary from 8 to 15, depending on the duration of hydrogen pretreatment (Table 1). 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 [12]. For alumina, prepared by sol–gel method, hydrogen spillover from small palladium particles was reported [13]. 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 [14], or ceria [7].

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 [15]. 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 ($8 \leq H/Pd \leq 15$) 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 H/Pd is near 0.1 for hydrogen absorption at room temperature under atmospheric pressure for very small palladium particles [16]. This value is negligibly small, as compared to observed ratios, varied from 8 to 15.

4.3. Catalytic reaction

Sol–gel Pd/Al_2O_3–La_2O_3 catalysts reach total conversion of NO at temperature 473 K that is 150° lower than Pd/Al_2O_3 catalysts. In contrast, coprecipitated Pd/Al_2O_3–La_2O_3 catalysts do not reach total NO conversion even at 973 K. Hence, preparation method significantly influences the catalytic activity of Pd/Al_2O_3–La_2O_3 catalysts. Sol–gel Pd/Al_2O_3–La_2O_3 catalysts exhibit no inflection of the NO conversion at any temperature in contrast to Pd/Al_2O_3 ones which show that NO conversion first increases with temperature, then decreases before passing through a minimum at 423–473 K. By this reason, sol–gel Pd/Al_2O_3–La_2O_3 catalysts show higher catalytic activity than Pd/Al_2O_3 catalysts in the range 473–623 K. NO conversion of coprecipitated Pd/Al_2O_3–La_2O_3 catalysts also exhibits a minimum. However, its minimum is not so pronounced and is observed at 773 K that is 300–350 K higher than the minimum of Pd/Al_2O_3. It can be suggested that reduction of lanthana in intimate contact with well-dispersed palladium is responsible for this behavior. Existence of the activity drop on coprecipitated Pd/Al_2O_3–La_2O_3 catalysts is probably due to lack of such good contact in the samples prepared by method of coprecipitation.

On sol–gel Pd/Al_2O_3–La_2O_3 catalysts at temperatures higher than 523 K nitrogen, concentration remains constant in contrast to coprecipitated Pd/Al_2O_3–La_2O_3 and Pd/Al_2O_3 catalysts which showed that nitrogen concentration increases with temperature. For ammonia concentration the difference between lanthana promoted and non-promoted catalysts is very pronounced. At temperatures higher than 673 K either sol–gel or coprecipitated $Pd/Al_2O_3–La_2O_3$ catalysts yields ca. 80% ammonia concentration while Pd/Al_2O_3 catalysts yielded $<$50%.

Sol–gel and coprecipitated $Pd/Al_2O_3–La_2O_3$ 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.

Temperature range of N_2O existence in the reaction mixture is 323–523, 373–673 and 373–623 K on sol–gel $Pd/Al_2O_3–La_2O_3$, coprecipitated $Pd/Al_2O_3–La_2O_3$ and Pd/Al_2O_3 catalysts, respectively. Hence, the range is narrower and shifted to lower temperature on sol–gel $Pd/Al_2O_3–La_2O_3$ catalyst compared with coprecipitated $Pd/Al_2O_3–La_2O_3$ and Pd/Al_2O_3 catalysts.

Results on sol–gel lanthana–alumina support without palladium showed that at high temperatures (>673 K) conversion of NO occurs with predominant formation of ammonia (Fig. 4). The temperatures of initiation of the reaction and reduction of lanthana essentially coincide (550 K, Figs. 1 and 4). An agreement also exists between temperatures of the end of sample reduction (700 K, Fig. 1) and maximum of ammonia production (773 K, Fig. 4). These data suggest that reduced sites of lanthana are able to reduce NO in presence of hydrogen. Ammonia selectivity is ca. 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.

On the basis of results obtained for pure sol–gel $Al_2O_3–La_2O_3$ support it is believed that the addition of palladium to lanthana–alumina phase 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 ca. 300 K lower than that on sol–gel $Al_2O_3–La_2O_3$ support.

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.

Coprecipitated $Al_2O_3–La_2O_3$ support without Pd showed similar activity towards N_2 and N_2O but essentially lower (ca. order of magnitude) towards NH_3 (Fig. 4). To explain this difference additional experiments are needed.

4.4. TEM and XRD

The interplanar distances measured in HRTEM micrographs of $Al_2O_3–La_2O_3$ samples for shapeless aggregates are 0.334 and 0.326 nm with angle $\sim 72°$; 0.296 and 0.262 nm with angle $\sim 85°$; 0.331 and 0.295 nm with angle $\sim 79°$ (Fig. 7, zones A, B, and C, respectively). Interplanar spacings of the new phase calculated from X-ray diffractograms of lanthana-containing samples (Fig. 5) were close to 0.330, 0.292 and 0.264 nm. This similarity suggests that the ‘dark clouds’ observed by TEM correspond to the new phase, detected by XRD. Attempts to match new crystalline phase to any of the cards in the ICDD-PDF database [17], related with La, Al or La–Al oxides, were unsuccessful.

The new phase is very stable in different atmospheres at relatively high temperature:

1. in hydrogen flow at 673 K for 8 h
2. in nitrogen flow at 723 K for 12 h; and
3. in air after Pd supporting followed by heating at 873 K for 3 h.

An X-ray diffraction pattern similar to that of the new phase was observed by Mizukami et al. [18] for $Al_2O_3–La_2O_3$ (10% La_2O_3), prepared by sol–gel technique, calcined at 1473 K for 3 h. These authors did not interpret their published diffractogram.

For coprecipitated $Al_2O_3–La_2O_3$, X-ray diffraction pattern is typical for γ-Al_2O_3 (Fig. 5). The peaks of new phase (detected in the diffractograms of sol–gel $Al_2O_3–La_2O_3$) were not found in the diffractograms of coprecipitated $Al_2O_3–La_2O_3$. In the TEM micrographs of coprecipitated $Al_2O_3–La_2O_3$, high contrast shapeless aggregates were not found either. Hence, we can conclude that coprecipitation does not bring to the formation of new phase detectable by XRD.

4.5. XPS

Values of O 1s and Al 2p binding energies for all samples studied are close to those of γ-Al_2O_3 [19].

Pd $3d_{5/2}$ binding energy 336.1–336.2 eV, registered for 0.3% $Pd/Al_2O_3–La_2O_3$, can be assigned to ionic palladium (palladium oxides or palladium incorporated into support lattice) or to small metallic palladium particles. Palladium clusters with a diameter near 1 nm in Pd/Al_2O_3 present a Pd $3d_{5/2}$ binding energy 0.8 eV higher than bulk Pd [20]. The difference between Pd $3d_{5/2}$ binding energy for 0.3% $Pd/Al_2O_3–La_2O_3$ and 2% Pd/Al_2O_3 is ca. 1.6 eV [5]. This suggests that in the case of the 0.3% $Pd/Al_2O_3–La_2O_3$ sample both these reasons (palladium oxidation and particle size effect) should be taken in to account. Palladium particles in 0.3% $Pd/Al_2O_3–La_2O_3$ are small and oxidized. Under reduction conditions of this work, palladium particles in both studied catalysts did not change their state of oxidation.

As far as lanthanum oxidation state is concerned, in sample of La_2O_3 the $3d_{5/2}$ binding energy of lanthanum was 835.1 eV, that is typical for this compound [19]. For $Al_2O_3–La_2O_3$ and 0.3% $Pd/Al_2O_3–La_2O_3$, the $3d_{5/2}$ binding energy of lanthanum was 836.0–836.2 eV. According to Ref. [19], this energy is characteristic for metallic lanthanum. It is difficult to suggest that lanthanum is in the metallic state in these samples. Nevertheless, the relatively high energy shift for the binding energy of lanthanum ($\Delta = 1$ eV) for $Al_2O_3–La_2O_3$ and for 0.3% $Pd/Al_2O_3–La_2O_3$ can be considered as a clear evidence of lanthana reduction. This shift is diminished ($\Delta = 0.4$ eV) for $Al_2O_3–La_2O_3$ calcined at 1273 K.

In the spectrum of dried $Al_2O_3–La_2O_3$, besides the peak at 836.5 eV, another peak, typical for La^{3+} (834.6 eV) was observed as a shoulder. It could be originated from the coexistence of two lanthanum-containing compounds before the heat treatment. One of them seems to be La_2O_3 (834.6 eV) and the other (836.5 eV) is suggested to be the new lanthanum-containing phase. Hence, the data of XRD, HRTEM and XPS demonstrated the formation of a new lanthana-containing phase besides γ-Al_2O_3 in sol–gel alumina–lanthana mixed support. The lanthanum state in the new phase is more reduced than in La_2O_3 compound.

On coprecipitated $Pd/Al_2O_3–La_2O_3$ catalyst the character of the changes of the concentrations of NO and products with time is very similar to ones for Pd/Al_2O_3 catalyst. NO conversion reaches 100% on sol–gel $Pd/Al_2O_3–La_2O_3$ and Pd/Al_2O_3 catalyst at 473 and 623 K, respectively. However, on coprecipitated $Pd/Al_2O_3–La_2O_3$ catalyst, NO conversion does not reach 100% even at 973 K. Hence, activity of Pd/Al_2O_3 catalyst is improved at medium temperature with lanthana addition by sol–gel method, but significantly decreases with lanthana addition by coprecipitation. According to XRD data, coprecipitated $Pd/Al_2O_3–La_2O_3$ catalyst does not contain new lanthanum-containing phase. These data confirm suggestion that new phase is responsible for observed change of catalytic behavior of sol–gel lanthana-promoted palladium catalysts.

An activity change caused by lanthana promotion may take place at temperatures when reduction of lanthana occurs. XPS data of the present work revealed, that the state of lanthanum in $Al_2O_3–La_2O_3$ and 0.3% $Pd/Al_2O_3–La_2O_3$ is more reduced than in La_2O_3. The above arguments confirm that the lanthanum-containing phase changes adsorption and catalytic properties due to easiness of reduction of lanthana. It results in:

1. an ability to consume hydrogen in excess above that necessary for complete PdO reduction because it is spent for La_2O_x reduction;
2. essential enhanced hydrogen consumption (H/Pd up to 15) because of hydrogen spillover to the support and lanthana reduction;
3. similar character of reduction of NO by H_2 at low temperatures comparable to non-promoted Pd/Al_2O_3 catalysts [4] but higher activity at intermediate temperatures (when lanthana can be reduced and prevent reduction of palladium oxide particles) and enhanced ammonia selectivity at elevated temperatures (because of enhanced hydrogen adsorption and NO dissociation).

One of the probable mechanism of lanthana influence might be change of the catalyst acid properties and further experiments are needed for the mechanism study.

5. Conclusions

A crystalline lanthanum-containing phase is registered with XRD and HRTEM in $Al_2O_3–La_2O_3$ and $Pd/Al_2O_3–La_2O_3$ samples prepared by sol–gel method. This lanthanum-containing phase is suggested to be responsible for the modification of the catalytic properties of sol–gel Pd/Al_2O_3–La_2O_3 as compared to Pd/Al_2O_3 in the reduction of NO by hydrogen. It improves the catalytic activity at medium temperature and increases the selectivity to NH_3 at high temperatures. In contrast, coprecipitated Al_2O_3–La_2O_3 and Pd/Al_2O_3–La_2O_3 samples do not contain the crystalline lanthanum-containing phase registered for sol–gel samples. The activity on coprecipitated Pd/Al_2O_3–La_2O_3 catalyst is lower than on sol–gel Pd/Al_2O_3–La_2O_3 and Pd/Al_2O_3 ones at temperature up to 973 K. The increase in NH_3 production decreases practical value of the lanthanum-promoted catalysts for a NO reduction catalyst.

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