PURIFICATION OF GASOLINE EXHAUST GASES USING BIMETALLIC PD-RH/Δ-AL2O3 CATALYSTS

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Abstract - In the present work, a series of palladium- and rhodium-containing samples supported on delta-alumina was prepared. Monometallic samples containing corresponding metal loading serve as the references. Catalytic performance of the catalyst was studied in three-way catalysis under both the stoichiometric and reductive conditions. Thermal stability was examined using a prompt thermal aging procedure. The samples were characterized by means of luminescence and UV-vis spectroscopies, since due to low metal loading the most of other characterization techniques was not applicable. All the samples were found to undergo deactivation during the aging. At the same time, for bimetallic Pd-Rh systems an effect of reactivation was observed at 800 °C. Then, being subjected to the treatment at 1000 °C, these samples showed a rapid agglomeration of the active particles.

Index Terms - Bimetallic Pd-Rh alloys, luminescence spectroscopy, thermal stability, three-way catalysts, UV-vis spectroscopy.

I. INTRODUCTION

Regarding the historical facts, the first internal combustion engine was created in 1876 in Germany. Almost a hundred years later, the automotive exhaust catalysts developed in aim to neutralize the pollutant emissions from cars were commercialized [1[, [2]. The main pollutants from the gasoline engines are represented by carbon monoxide, unburnt hydrocarbons and nitrogen oxides. During the 40 years of development, the exhaust gas after-treatment systems have been progressed with significant improvement following the toughened legislative restrictions in pollutant control [3]-[8].

Nowadays, the catalytic converter is represented by a cordierite brick of honeycomb structure coated with the active layers. The number of layers can be varied depending on their exact composition. Thus, they contain secondary oxide support (Al_2O_3, CeO_2, ZrO_2 or complex compositions based on the mentioned oxides with other additives). Metals of platinum group (Pt, Pd, Rh) supported on these oxides are responsible for the catalytic utilization of the contaminants. However, the active components become to be really active only at temperatures above light-off temperature, which usually lies within a range of 150 – 200 °C. Since the temperature of the exhaust gases at the engine start is lower than these values, so-called 'cold start' problem appears. In order to solve the problem, such hydrocarbons' traps as zeolites are often added into the composition of catalytic converter [9]. The trapping component provides adsorption of unburnt hydrocarbons at the beginning with subsequent desorption, when the temperature of exhaust gases reaches light-off value. At temperatures above 200 °C, the main functions of the three-way catalyst are as follows: the oxidation of unburnt hydrocarbons; the oxidation of carbon monoxide; the reduction of nitrogen oxides. Platinum and palladium are known to catalyze well the oxidation processes, while an addition of rhodium is required to provide the reduction function [10], [11].

On the other hand, the temperature of the exhaust gases during the engine operation can achieve as high values as 1000 °C. Such a drastic condition facilitates the deactivation processes to take place. These processes are mostly connected with changes in the oxide support (phase transformation, collapse of the porous structure, sintering, etc.), changes in the active components (agglomeration of the palladium particles, bulk diffusion of rhodium ions, etc. [12], [13]) or loss of the wash-coat components. The latter problem can be solved by an addition of the binding agents into the initial composition in order to provide its better adhesion and mounting on the surface of the cordierite brick. Doping of the oxide supports with La_2O_3, ZrO_2 and some other oxides significantly improves their thermal stability [14]-[16]. It should be also noted that one of the most important properties for the three-way catalysis is an oxygen storage capacity (OSC) of the support. The OSC function is known to be performed by the lanthanide oxides, and CeO_2 is the most commonly used one among them [17]. Thereby, the supports for the modern three-way catalysts are not the individual oxides. They are represented by a complex mixture of various oxides.

Another important point is stabilization of the active components. As it was reported recently, the stabilization effect can be reached by using the bimetallic Pd-Rh systems [18]-[25]. It should be emphasized that the low loading of platinum group metals is also important, since it corresponds to concentration of electron donor sites on the surface of the support. In this case, an improved anchoring of palladium on the support takes place that prevents its surface migration and agglomeration. The concentration of such sites, measured by an electron spin resonance (ESR) spectroscopy [26], was shown to be noticeable in the cases of γ-alumina and zirconia [12], [27], [28].

Taking into account all the mentioned above, the present work was aimed to elucidate in detail the effects of metal-metal and metal-support interactions in the bimetallic Pd-Rh/δ-Al_2O_3 system. Delta phase of alumina was chosen as a support, which is not expected to undergo any phase transformations at the operation temperatures (up to 1000 °C). In practice, δ-Al_2O_3 is quite often used in the composition of various catalysts as a support combining both the large enough specific surface area and the excellent thermal stability [29]-[34]. The prepared samples were tested under the TWC conditions. Thermal stability was examined in a model reaction of CO oxidation in a prompt thermal aging regime. Characterization of the samples was performed using optical methods (diffuse reflectance UV-vis spectroscopy, luminescence spectroscopy).

II. EXPERIMENTAL

A. Preparation of the samples

δ-Al_2O_3 support used in this research was prepared by calcination of commercial $Al(OH)_3$ hydroxide (Condea) for 6 h at 1000 °C. Prior the calcination the oven was heated up from room temperature with ramping rate of 1.5 °C/min. An incipient wetness impregnation of the support with a dual complex salt $[Pd(NH_3)_4]_3$ $[Rh(NO_2)_6]_2$ was used to obtain alloyed Pd-Rh catalysts. The total metal loading in the prepared samples was 0.2 wt. %. The impregnated samples were dried in a furnace at 105 °C for 4 h, then heated in air at 400 °C at the heating rate 10 °C/min, and allowed to stay for 1 h at this temperature. The calcined samples were triply boiled in distilled water, filtered out of $NaNO_3$ using a porous filter and dried in a furnace at 105 °C for 4 h. The atomic Pd:Rh ratio in the prepared samples was varied within three following values: 3:2, 7:3 and 4:1. These samples were designated as PdRh32(alloy), PdRh73(alloy) and PdRh41(alloy), correspondingly.

The reference bimetallic samples were synthesized by a separate incipient wetness impregnation of identical weighted alumina samples with solutions of simple complexes $[Pd(NH_3)_4](NO_3)_2$ and $Na_3[Rh(NO_2)_6]$. The concentrations of deposited metals were 0.24, 0.28, 0.32 wt.% and 0.16, 0.12, 0.08 wt.%, respectively, to maintain the identical ratio and concentrations of the metals in their mechanical mixture. The samples were dried and calcined using the procedures described above. Then, they were thoroughly ground in an agate mortar for homogenization. These samples were labeled as PdRh32(mix), PdRh73(mix) and PdRh41(mix), correspondingly.

The monometallic reference samples containing 0.12, 0.14, 0.16 wt.% Pd and 0.08, 0.06, 0.04 wt.% Rh were synthesized using the same procedure. They were designated as Pd32(mono), Pd73(mono), Pd41(mono), Rh32(mono), Rh73(mono) and Rh41(mono), respectively.

B. Characterization of the samples

Photoluminescence experiments were carried out under atmospheric conditions at 290 K using a Cary Eclipse (Varian) spectrofluorimeter. A powder sample was placed in a 0.8 mm UV quartz cell in a front-face configuration.

UV-vis diffuse reflectance spectra were recorded between 190 and 900 nm using a UV-vis spectrometer UV-VIS 2501 PC (Shimadzu) with IRS-250A diffusion reflection attachment. The UV–vis spectra were transformed into the Kubelka–Munk function F(R) calculated as $F(R) = (1 - R)^2/2R$, where R is the experimentally measured reflectivity coefficient of the samples [35]. All the samples were studied in relation to pure support calcined at the same temperature. The spectra were normalized in amplitude to 1.0 in the area of d-d transition for Pd^{2+}.

C. Examination of catalytic activity and thermal stability

Light-off testing of the catalysts was performed using a flow fixed bed reactor equipped with a mass-spectrometer GMS-200 as described elsewhere [36], [37]. The experiments were carried out in 4 heating–cooling cycles. Air to fuel ratio (λ) for the first three cycles was set to be 1.003 (stoichiometric conditions), for the forth cycle it was 0.95 (reductive conditions). The parameters of light-off tests are listed below: temperature ramping rate - 10 °C/min; space velocity - 240,000 h^{-1}; catalyst loading - 0.250 cm^3; contact time - 0.015 s; temperature range - from 100 to 500 °C. The reaction mixture consisted of 0.30 vol.% CO, 0.31 vol.% O_2, 0.035 vol.% C_3H_6, 0.015 vol.% C_3H_8, 0.15 vol.% NO, 10.0 vol.% H_2O, and He as balance.

The thermal stability of the samples was studied using

an in situ prompt thermal aging (PTA) procedure as described elsewhere [36]-[38]. CO conversion was used as a chemical response to follow both catalytic behavior and state of active components during the procedure. The temperature of 50% CO conversion (T_{50}) was used as the criterion to compare the catalysts. The sample (300 mg) was loaded into quartz flow reactor, and then reaction mixture contained 0.15 vol. % CO, 14.0 vol. % O_2 and N_2 as balance was passed through the reactor. The flow rate was 334 ml/min. Temperature ramping rate was 10 °C/min. The samples underwent two light-off cycles at 50-320 °C, two cycles at 50 – 600 °C, and finally three cycles at 50-800 °C. Changes in the CO concentration in the outlet flow were registered by a gas analyzer ULTRAMAT 6 (Siemens).

Additionally, all the samples were subjected to a conventional thermal aging procedure. Each sample was placed into quartz flow reactor and heated up to 800 or 1000 °C with ramping rate of 10 °C/min under the same reaction condition. The duration of high temperature step was 6 h.

III. RESULTS AND DISCUSSIONS

A. Catalytic activity of the samples

All the prepared samples were studied under the conditions of three-way catalysis. Each sample was subjected to three light-off tests at near stoichiometric conditions (λ=1.003) and one test at reductive conditions (λ=0.95). Fig. 1 shows light-off curves for 3rd and 4th runs over PdRh32(alloy) sample, as an example. As seen, the difference in activity at stoichiometric and reductive conditions is insignificant. In the most cases, the light-off curves coincide with each other. At the same time, since the activity under reductive conditions is little bit worse, these conditions were used for further consideration. As a criterion of activity, the temperature of 50% conversion (T_{50}) was used. T_{50} values for conversion of CO, propane, propylene and NO for all the bimetallic and monometallic reference samples are summarized in Table 1. As it follows from the presented data, in the case of bimetallic PdRh(alloy) samples, an increase of palladium loading worsens the activity in oxidation of CO and propylene and in reduction of NO.

The activity in propane oxidation slightly increases and stabilizes at T_{50} value of 430 °C for Pd:Rh ratios of 7:3 and 4:1. The reference bimetallic PdRh(mix) catalysts show the similar tendencies: the activity falls down in all the processes including oxidation of propane. In general, the bimetallic alloyed catalysts presents better catalytic performance if compare with the bimetallic mixed reference samples.

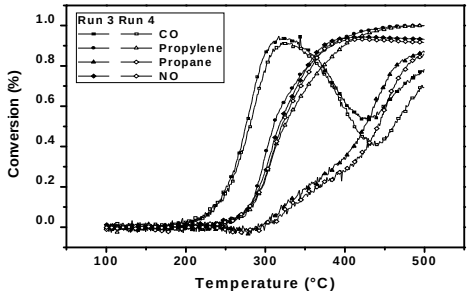


Fig. 1. Light-off curves for oxidation of CO, propane and propylene, and reduction of NO under stoichiometric (Run 3) and reductive (Run 4) conditions over PdRh32(alloy) sample.

The observed tendencies are in good agreement with the behavior of the monometallic Pd(mono) samples, which are the worst ones within all the studied samples under the applied reaction conditions. It should be noted that the catalytic performance of the monometallic Rh(mono) samples is very similar to that for the reference bimetallic PdRh(mix) samples. It indicates the absence of metal-metal interaction in bimetallic PdRh(mix) catalysts, which behavior is mostly defined by more active rhodium. Since the performance of PdRh(alloy) samples is different, it confirms a presence of strong metal-metal interaction in this case.

Table 1. Temperatures of 50% conversion of CO, propane propylene and NO over the bimetallic and monometallic samples under reductive conditions.

Sample	T_{50} (°C)			
	CO	C_3H_6	C_3H_8	NO
PdRh32(alloy)	281	324	441	320
PdRh73(alloy)	292	343	430	360
PdRh41(alloy)	306	347	432	375
PdRh32(mix)	251	289	423	286
PdRh73(mix)	260	302	437	298
PdRh41(mix)	269	316	448	306
Pd32(mono)	480	355	430	414
Pd73(mono)	483	354	429	416
Pd41(mono)	471	350	423	405
Rh32(mono)	250	301	427	296
Rh73(mono)	253	304	433	299
Rh41(mono)	264	313	449	305

B. Thermal stability of the samples

Thermal stability of the samples was studied in an in situ prompt thermal aging regime using CO conversion as a chemical response. As an example, light-off curves for CO oxidation over PdRh32(alloy) sample in seven consecutive runs are presented in Fig. 2. The 1st run shows activity of the fresh sample, which is usually much higher comparing with other runs. The position of curve for the 3rd run corresponds to a steady-state of the catalyst treated at 320 °C. Then, heating up to 600 and 800 °C shifts the light-off curves towards higher T_{50} values, and the positions of 5th and 7th curves indicate the steady-state activity of the

catalyst at these conditions. Thereby, values of T_{50} for CO conversion in 3rd, 5th and 7th runs for all the studied samples are plotted in Fig. 3. Fluctuations of these values reflect the deactivation or reactivation processes taking place during the treatment under applied thermal aging conditions.

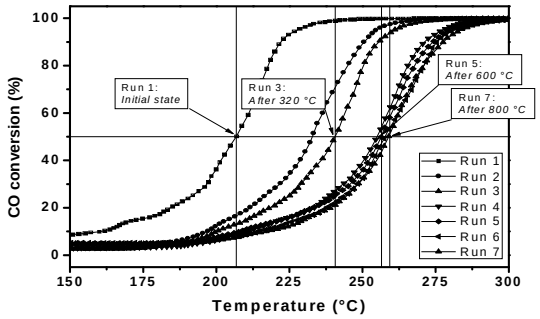


Fig. 2. Light-off curves for CO oxidation over PdRh32(alloy) sample in 7 consecutive catalytic runs under prompt thermal aging conditions.

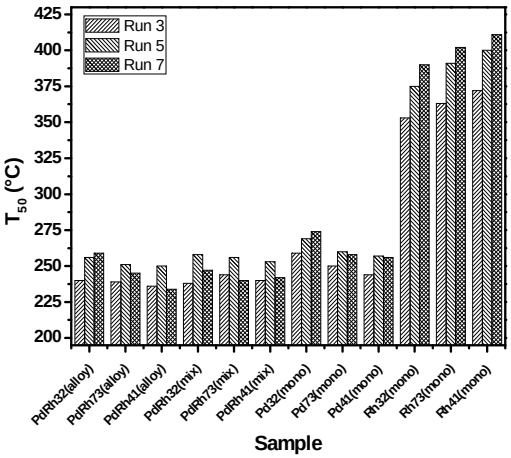


Fig. 3. Temperature of 50% CO conversion (T_{50}) in 3rd, 5th and 7th catalytic runs under prompt thermal aging conditions for all the studied samples.

Since the prompt thermal aging conditions consider oxygen excess, palladium-containing catalysts show better activity comparing with monometallic rhodium samples. Moreover, it is well seen that Rh(mono) catalysts undergo significant deactivation from run to run. As it was reported recently, this deactivation is caused by diffusion of Rh^{3+} ions into the bulk of alumina [13], [38]. In the case of monometallic palladium samples, an increase of Pd loading results in formation of more active and more stable catalysts. The T_{50} values in 5th and 7th runs for Pd73(mono) and Pd41(mono) samples were almost the same. Surprisingly, in the case of bimetallic PdRh(alloy) and PdRh(mix) series, an effect of reactivation after treatment at 800 °C was observed. This effect is the most significant for the PdRh41(alloy) sample, which showed better T_{50} value in 7th run comparing with 3rd run (234 and 236 °C, correspondingly).

C. UV-vis spectroscopic characterization of the samples

A diffuse reflectance UV-vis spectroscopy was recently shown to be very effective tool to study the dispersity and the state of low-loaded Pd- and Rh-containing catalysts. The characteristic spectra for the bimetallic and monometallic reference samples are demonstrated in Fig. 4. The initial state of the Pd-containing catalysts is characterized by a metal-ligand charge transfer transition at 280 nm and d-d bands at 415 nm corresponding to isolated ionic Pd^{2+} species and oxide cluster of small size hydroxylated under the atmospheric conditions [39]. The observed position of d-d transitions corresponds to the $Pd(OH)_4^{2-}$ complexes [40]. As seen from Fig. 4, there is no big difference between in spectra for the samples treated at 400 °C. At the same time, the samples of PdRh(alloy) series are characterized with slightly better dispersity of the palladium species if compare with reference PdRh41(mix) and Pd41(mono) samples (spectra 4 and 5).

The situation has changed significantly after the treatment at elevated temperatures. Fig. 5 compares spectra for bimetallic PdRh41(alloy) sample treated at 400, 600, 800 and 1000 °C. This sample was chosen, since it showed better reactivation effect during the prompt thermal aging procedure (Fig. 3). As it follows from the presented spectra, a redispersion of the PdO particles with formation of dispersed palladium species takes place at temperatures of 600-800 °C. Calcination of the sample at 1000 °C changes the situation dramatically (Fig. 5, spectrum 4). An agglomeration of palladium into large PdO and Pd^0 particles is well seen. Thereby, Pd-Rh/ δ-Al_2O_3 catalyst with Pd:Rh ratio of 4:1 shows significant metal-metal interaction and reactivation effect at temperatures near 800 °C, but undergoes rapid deactivation at 1000 °C caused by palladium agglomeration. The observed deactivation is most probably connected with weak metal-support interaction.

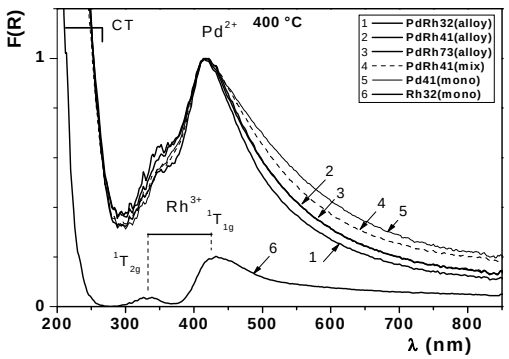


Fig. 4. Diffuse reflectance UV-vis spectra for bimetallic PdRh(alloy), PdRh41(mix) and monometallic reference samples calcined at 400 °C.

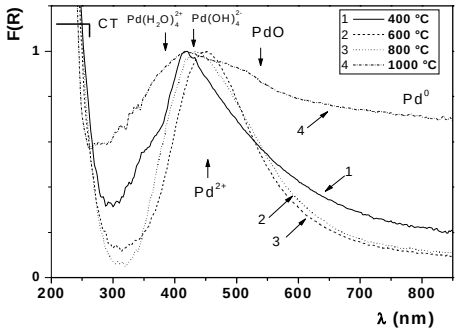


Fig. 5. Diffuse reflectance UV-vis spectra for PdRh41(alloy) sample treated at varied temperatures.

D. Luminescence spectroscopic studies

Finally, all the bimetallic systems were characterized by a luminescence spectroscopy (Fig. 6). This study supplements the UV-vis data, since UV-vis spectra for bimetallic systems were defined by palladium (Fig. 4, spectra 1 and 6). Luminescence spectroscopy was recently reported to be efficient for measuring the concentration of rhodium ions diffused into the bulk of alumina. It is important to note that the characterization of the Rh-containing samples based on pure (non-promoted) alumina support is applicable only after calcination at temperatures near 1000 °C, when diffused Rh^{3+} ions initiate formation of corundum phase [13], [38]. In the α-Al_2O_3 structure, Rh^{3+} ions occupying low-spin octahedral positions are characterized by a phosphorescence band at 650 nm. The method allows one to control the amount of Rh^{3+} ions in α-Al_2O_3 as well as trace amounts of θ- and α-phases of alumina in the bulk of the support (using the luminescence of impurity Cr^{3+} ions).

Fig. 6 demonstrates the luminescence spectra for bimetallic PdRh(alloy) and PdRh(mix) catalysts after calcination at 1000 °C. In the case of samples with Pd:Rh ratio of 4:1, no difference in spectra for alloyed and mixed samples was observed. It testifies towards similar deactivation mechanisms and equal amount of diffused rhodium species for these samples. A decrease of palladium content in the Pd-Rh alloy strengthens the metal-metal interaction that leads to better stability of the system at 1000 °C and corresponds to less amount of diffused rhodium.

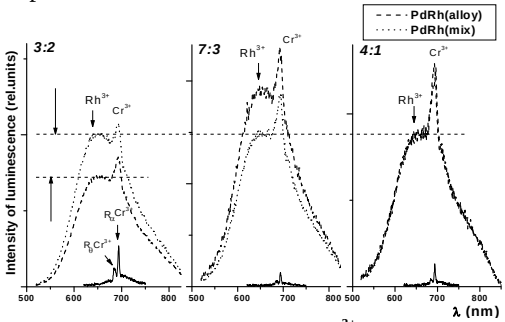


Fig. 6. Photoluminescence spectra for Rh^{3+} ions in PdRh(alloy) and PdRh(mix) samples after aging at 1000 °C with Pd:Rh ratio of 3:2, 7:3 and 4:1 at excitation λ_{ex}=390 nm, and for Cr^{3+} ions at excitation λ_{ex}=565 nm. The spectra were plotted with consideration of different optical density of the samples.

CONCLUSION

In the present work, the detailed study of bimetallic Pd-Rh/δ-Al_2O_3 catalysts in comparison with monometallic reference samples was performed. It was shown that the catalysts are characterized with a weak metal-support interaction. At the same time, all the alloyed samples possess a metal-metal interaction, which strength is increased with decrease of palladium loading. PdRh32(alloy) system was found to be the most stable at 1000 °C due to the strongest metal-metal interaction. Oppositely, PdRh41(alloy) sample characterized with the weakest metal-metal interaction has showed more evident reactivation effect at temperatures near 800 °C due to redispersion of the palladium species. Calcination of this sample at 1000 °C has led to decomposition of alloy, agglomeration of palladium species into large PdO and Pd^0 particles and diffusion of rhodium into the bulk of alumina.

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REFERENCES

[1] M. Shelef, and R. W. McCabe, “Twenty-five years after introduction of automotive catalysts: what next?” Catal. Today, vol. 62, pp. 35-50, Sept. 2000.

[2] H. S. Gandhi, G. W. Graham, and R. W. McCabe, “Automotive exhaust catalysis,” J. Catal., vol. 216, pp. 433-442, May-June 2003.

[3] M. V. Twigg, “Controlling automotive exhaust emissions: successes and underlying science,” Philosophical Transactions of the Royal Society of London, Series A: Mathematical, Physical and Engineering Sciences, vol. 363, pp. 1013-1033, April 2005.

[4] M. V. Twigg, “Catalytic control of emissions from cars,” Catal. Today, ,vol. 163, pp. 33-41, April 2011.

[5] S. Matsumoto, “Advances in automobile exhaust catalyst,” Studies in Surface Science and Catalysis, vol. 172, pp. 27-34, August 2007.

[6] D. Chatterjee, V. Schmeisser, M. Frey, and M. Weibel, “Perspectives of the automotive industry on the modeling of exhaust gas aftertreatment catalysts,” in “Modeling and Simulation of Heterogeneous Catalytic Reactions,” O. Deutschmann (Ed.), pp. 303-343, Dec. 2011.

[7] B. Gokalp, “Using the three-way catalyst monolith reactor for reducing exhaust emissions,” J. Renew. Sustain. Energy, vol. 4(4), pp. 043114/1-043114/21, July 2012.

[8] O. Deutschmann, and J.-D. Grunwaldt, “Exhaust gas after-treatment in mobile systems: Status, challenges, and perspectives,” Chemie Ingenieur Technik, vol. 85, pp. 595-617, March 2013.

[9] V. Temerev, A. Vedyagin, K. Iost, T. Afonasenko, and P. Tsyrulnikov, “Enhanced Adsorption Properties of Ag-Loaded β-Zeolite towards Toluene,” Mater. Sci. Forum, vol. 917, pp. 180-184, March 2018.

[10] K. C. Taylor, “Nitric oxide catalysis in automotive exhaust systems,” Catal. Rev. Sci. Eng., vol. 35, pp. 457-481, April 1993.

[11] M. Shelef, and G. W. Graham, "Why rhodium in automotive three-way catalysts," Catal. Rev. Sci. Eng., vol. 36, pp. 433-457, March 1994.
[12] A. Vedyagin, A. M. Volodin, V. O. Stoyanovskii, I. V. Mishakov, D. A. Medvedev, and A. S. Noskov, "Characterization of active sites of Pd/Al2O3 model catalysts with low Pd content by luminescence, EPR and ethane hydrogenolysis," Appl. Catal. B-Environ., vol. 103, pp. 397-403, April 2011.
[13] V. O. Stoyanovskii, A. A. Vedyagin, G. I. Aleshina, A. M. Volodin, and A. S. Noskov, "Characterization of Rh/Al2O3 catalysts after calcination at high temperatures under oxidizing conditions by luminescence spectroscopy and catalytic hydrogenolysis," Appl. Catal. B-Environ., vol. 90, pp. 141-146, July 2009.
[14] H. Ni, Y. Guo, L. Wang, Y. Guo, W. Zhan, and G. Lu, "Facile synthesis of highly thermal-stable doped alumina with high surface area by low temperature solid-state reaction," Powder Technol., vol. 315, p. 22-30, June 2017.
[15] Kadari, K. Mahi, L.O. Faria, B. Saoula, and B. Adila, "Study of the physical properties of amorphous Zr doped Al2O3 powders," Chin. J. Phys., vol. 55, pp. 127-132, Feb. 2017.
[16] L. Lallemant, N. Roussel, G. Fantozzi, V. Garnier, G. Bonnefont, T. Douillard, B. Durand, S. Guillemet-Fritsch, J.-Y. Chane-Ching, D. Garcia-Gutierez, and J. Aguilar-Garib, "Effect of amount of doping agent on sintering, microstructure and optical properties of Zr- and La-doped alumina sintered by SPS," J. Europ. Ceram. Soc., vol. 34, pp. 1279-1288, May 2014.
[17] E. A. Alikin, and A. A. Vedyagin, "High temperature interaction of rhodium with oxygen storage component in three-way catalysts," Top. Catal., vol. 59, pp. 1033-1038, July 2016.
[18] A. Vedyagin, A. M. Volodin, R. M. Kenzhin, V. O. Stoyanovskii, Y. V. Shubin, P. E. Plyusnin, and I. V. Mishakov, "Effect of metal-metal and metal-support interaction on activity and stability of Pd-Rh/Alumina in CO oxidation," Catal. Today, vol. 293–294, pp. 73-81, Sept. 2017.
[19] S. B. Kang, S. B. Nam, B. K. Cho, I.-S. Nam, C. H. Kim, and S. H. Oh, "Effect of speciated HCs on the performance of modern commercial TWCs," Catal. Today, vol. 231, pp. 3-14, August 2014.
[20] Y. Wang, Y. Shen, Y. Zong, S. Zhu, and S. Shen, "Promotional effects of Co, Ni doping on catalytic performance of Pd-Rh based three-way catalyst for simultaneously removing C3H8, CO and NO from vehicle exhaust," Huanjing Gongcheng, vol. 33, pp. 62-68, Feb. 2015.
[21] W. J. Zhang, J. Hu, Y. Duan, Y. Duan, L. Su, and N. Zhao, "The effect of substrate volume on the catalytic behavior of Pd/Rh three-way catalysts," Advanced Materials Research, vol. 624, pp. 295-298, 2013 (Dec. 2012).
[22] X.-t. Wang, X.-q. Ma, C.-r. Qu, F.-y. Wu, and B. Xu, "Characteristics of Pd-Rh/CeO2/Al2O3 TWC for NOx and PAHs removal in flue gas of MSWI," International Conference on Materials for Renewable Energy & Environment, Shanghai, China, vol. 2, pp. 1129-1132, May 2011.
[23] Y. Reneme, F. Dhainaut, and P. Granger, "Kinetics of the NO/H2/O2 reactions on natural gas vehicle catalysts-Influence of Rh addition to Pd," Appl. Catal. B-Environ., vol. 111-112, pp. 424-432, Jan. 2012.
[24] X. Wu, L. Xu, and D. Weng, "The thermal stability and catalytic performance of Ce-Zr promoted Rh-Pd/γ-Al2O3 automotive catalysts," Appl. Surf. Sci., vol. 221, pp. 375-383, Jan. 2004.
[25] B. A. Kouadio, F. Mei, T. Li, and L. Pang, "High performance Pd–Rh/YBaCo4O7/γ-Al2O3 three-way catalysts for gasoil engine," J. Taibah University for Science, vol. 11, pp. 1306-1316, Nov. 2017.
[26] D. A. Medvedev, A. A. Rybinskaya, R. M. Kenzhin, A. M. Volodin, and A. F. Bedilo, "Characterization of Electron Donor Sites on Al2O3 Surface," Phys. Chem. Chem. Phys., vol. 14, pp. 2587-2598, Jan. 2012.
[27] A. Vedyagin, A. M. Volodin, R. M. Kenzhin, V. O. Stoyanovskii, V. A. Rogov, V. V. Kriventsov, and I. V. Mishakov, "The role of chemisorbed water in formation and stabilization of active sites on Pd/Alumina oxidation catalysts," Catal. Today, vol. 307, pp. 102-110, June 2018.
[28] A. Vedyagin, A. M. Volodin, R. M. Kenzhin, V. V. Chesnokov, and I. V. Mishakov, "CO Oxidation over Pd/ZrO2 catalysts: Role of support's donor sites," Molecules, vol. 21, pp. 1289, Sept. 2016.
[29] E. Marceau, H. Lauron-Pernot, and M. Che, "Influence of the metallic precursor and of the catalytic reaction on the activity and evolution of Pt(Cl)/δ-Al2O3 catalysts in the total oxidation of methane," J. Catal., vol. 197, pp. 394-405, Jan. 2001.
[30] E. Erdinç, B. Selen Caglayan, and A. Erhan Aksoylu, "Methane OSR over Pt-Ni/δ-Al2O3: Performance and power law type kinetics," Int. J. Hydrogen Energy, vol. 42, pp. 20568-20578, August 2017.
[31] R. Ardiyanti, S. A. Khromova, R. H. Venderbosch, V. A. Yakovlev, and H. J. Heeres, "Catalytic hydrotreatment of fast-pyrolysis oil using non-sulfided bimetallic Ni-Cu catalysts on a δ-Al2O3 support," Appl. Catal. B-Environ., vol. 117–118, pp. 105-117, May 2012.
[32] Bazyari, Y. Mortazavi, A. A. Khodadadi, L. T. Thompson, R. Tafreshi, A. Zaker, and O. T. Ajenifujah, "Effects of alumina phases as nickel supports on deep reactive adsorption of (4,6-dimethyl) dibenzothiophene: Comparison between γ, δ, and θ-alumina," Appl. Catal. B-Environ., vol. 180, pp. 312-323, Jan. 2016.
[33] V. González, J. Rostrup-Nielsen, K. Engvall, and L. J. Pettersson, "Promoted RhPt bimetallic catalyst supported on δ-Al2O3 and CeO2–ZrO2 during full-scale autothermal reforming for automotive applications: Post-mortem characterization," Appl. Catal. A-Gen., vol. 491, pp. 8-16, Feb. 2015.
[34] K. Furuta, A. Nishida, H. Yata, K. Narui, and Y. Kohtoku, "Catalytic properties of PdO/δ-Al2O3 catalysts prepared by hot isostatic pressing," Appl. Catal. A-Gen., vol. 164, pp. 149-157, Dec. 1997.
[35] H. P. Boehm, H. Knözinger. J. R. Anderson, and M. Boudart (Eds.), Catalysis-science and technology, vol. IV, Springer-Verlag, Berlin, 1983.
[36] A. Vedyagin, M. S. Gavrilov, A. M. Volodin, V. O. Stoyanovskii, E. M. Slavinskaya, I. V. Mishakov, and Y. V. Shubin, "Catalytic purification of exhaust gases over Pd–Rh alloy catalysts," Top. Catal., vol. 56, pp. 1008-1014, August 2013.
[37] A. Vedyagin, A. M. Volodin, V. O. Stoyanovskii, R. M. Kenzhin, E. M. Slavinskaya, I. V. Mishakov, P. E. Plyusnin, and Y. V. Shubin, "Stabilization of active sites in alloyed Pd–Rh catalysts on γ-Al2O3 support," Catal. Today, vol. 238, pp. 80-86, Dec. 2014.
[38] V. O. Stoyanovskii, A. A. Vedyagin, A. M. Volodin, R. M. Kenzhin, Y. V. Shubin, P. E. Plyusnin, and I. V. Mishakov, "Peculiarity of Rh bulk diffusion in La-doped alumina and its impact on CO oxidation over Rh/Al2O3," Catal. Commun., vol. 97, pp. 18-22, July 2017.
[39] B. Gaspar, and L. C. Dieguez, "Dispersion stability and methylcyclopentane hydrogenolysis in Pd/Al2O3 catalysts," Appl. Catal. A-Gen., vol. 201, pp. 241–251, July 2000.
[40] D. Tessier, A. Rakai, and F. Bozon-Verduraz, "Spectroscopic study of the interaction of carbon monoxide with cationic and metallic palladium in palladium–alumina catalysts," J. Chem. Soc., Faraday Trans., vol. 88, pp.741-749, Feb. 1992.

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