

Catalytic CO oxidation over oxide supported Pd catalysts

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Catalytic CO oxidation properties of systems composed of Pd nano-particles impregnated on various CeO₂, and ZnO powders were examined. Also catalysts with two metals, Pd and Ga, impregnated on aforementioned oxides were prepared and investigated. In this case, we were looking for occurrence of PdGa bimetallic phase and its eventual influence of catalytic activity. The nano-oxide substrates were prepared using soft chemical processing. Pd and Ga were loaded on oxide support via conventional impregnation method. Structure and properties of prepared materials were characterized using Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), BET method and gas flow reactor. It is concluded that the starting temperature of CO oxidation reaction is changed by the nano-structure and the composition of catalyst. CeO₂ loaded with Pd or PdGa proved best catalytic properties, but there must be taken big care on CeO₂ preparation conditions in order to improve its structure. Also further development of metals impregnation method is necessary. It is expected that these results can be applicable to a design of catalysts for a wet reforming reaction of fuel in fuel cells application.

Key words: Heterogeneous catalysis, Carbon monoxide, Cerium oxide, Zinc oxide, Palladium.

1. INTRODUCTION

CO oxidation on catalysts at low temperature is an important catalysis in the field of technological applications of industry. This reaction can be used to remove one of air pollutants CO produced by cigarettes smoking, burning of fossil fuels, and so on. Also a design of aforementioned catalysis is required for a development of high performance anode materials which lower an influence of CO poisoning on the electrode in fuel cells. The design of CO oxidation on anode materials is a key for a development of high quality electrodes in fuel cells application.¹

Interfacial systems and surface alloys are key materials for a design of heterogeneous catalysts. The catalysts for CO oxidation are mostly designed as supported nanoparticles of a transition metal, mostly Pd which is known for its good catalytic activity and the theory of CO oxidation kinetics on it is well described.²⁻⁸ In the above mentioned arrangement, the metal catalyst with high surface area and high activity for CO oxidation can be prepared using a small amount of metal element. But it is necessary to decrease the temperature of catalytic oxidation and to improve the activity at low temperature.

Therefore the metal is often combined with other one, such as Group-9 to Group-11 elements. Catalysts efficiency can also be substantially affected by the support. Oxide supports like Al₂O₃, MgO, ZnO, ZrO, SnO₂, CeO₂ or zeolite are widely used for this purpose. Sufficient selection of the oxide support and deposited metals can decrease the temperature of catalytic CO oxidation by hundreds of kelvin, but in the case of previously reported catalysts, it is still higher than cca. 300 °C.

When two kinds of metals are present in the catalyst, a bimetallic phase can be formed in the interface of two metals. The bimetallic interface exhibits a modification of the electronic structure and chemical properties of the individual components upon alloying and/or the geometrical arrangement of the constituent atoms,⁹⁻¹² this effect has relevance toward catalysis. Occurrence of bimetallic interaction and its effect on catalytic activity is not generally described, but was frequently observed for example in case of Pd-Al^{13,14} or Pd-Ag¹⁵.

Also other parameters like particle size, morphology and composition, metal substrate interaction¹⁶ and thermal stability of the catalyst should be examined for a lowering of CO oxidation temperature. Therefore, the influence of sample composition and preparation conditions on the catalysis should be taken into account. In the present study, the systematical experiments were performed to improve the catalytic properties.

Cerium dioxide (CeO₂) as a support for Pd particles was developed in this work. CeO₂ can significantly lower CO oxidation temperature¹⁷⁻¹⁹ as compared with other oxides such as Al₂O₃ or commercial available ZnO. It is because CeO₂ forms a nonstoichiometric oxides CeO_{2-x} (0 < x ≤ 0.5) in reducing atmosphere at elevated temperature, that can be reoxidized to CeO₂ when exposed to an oxidizing environment (such as oxygen or water vapor).^{20,21} It is concluded that the oxygen storage and oxygen release capacity in CeO₂ can lower CO oxidation temperature.

2. EXPERIMENTAL DETAILS

2.1 Sample preparation

In this study, the ZnO and CeO₂ powders were used as an oxide support. We have uncovered that CeO₂ powder

prepared via soft chemical processing way is of much better CO oxidation properties than commercially available ones. Therefore four CeO₂ powders thereafter noted #1-#4, were prepared. Ce(NO₃)₃·6H₂O was used as Ce precursor and (NH₄)₂CO₃ as precipitant. Time and temperature of aging of prepared solution were varying, they were 1h and 70 °C, 1h/70 °C, 10h/75 °C, 48h/75 °C for oxides #1-#4 respectively. After that precipitants were washed in water and ethanol for several times, dried in N₂ flow and after that calcined for 2h at 800 °C (700 °C in case of sample CeO₂ #1) in a O₂ flow of 370 ccm/min. The same ZnO as reported in reference No.22 was used.

Pd and Ga were deposited on oxides via conventional impregnation method^{22,23} using a Pd(C₅H₇O₂)₂ and Ga(C₅H₇O₂)₃ precursors. Afterwards, samples were reduced in for 2 hours at 300 °C in a 50 ccm/min. gas flow composed of 10% H₂ and 90% He. Different Pd and Ga weight concentration were impregnated on ZnO and CeO₂, see list of prepared samples in Table I.

Table I. List of prepared samples, its composition, temperature of starting CO oxidation in the first and second annealing sample and maximum CO conversion rate.

CeO ₂ #1	9,5	---	160	---	72
CeO ₂ #2	9,5	---	120	---	74
CeO ₂ #3	3,7	---	240	240	91
CeO ₂ #3	13,9	---	210	210	93
CeO ₂ #3	---	8,0	neg.*	neg.*	neg.*
CeO ₂ #3	3,7	3,7	240	240	93
CeO ₂ #4	3,7	---	260	210	92
ZnO	3,7	---	250	240	93
ZnO	9,5	---	240	200	92
ZnO	---	3,8	neg.*	neg.*	neg.*
ZnO	4,8	1,6	175	190	65
ZnO	3,0	2,3	175	175	65

* neg. means that the CO oxidation activity is negligible, therefore the value cannot be assigned.

2.2 Experimental techniques

Surface area of ZnO and CeO₂ #3 and #4 was determined using a BELSORP 28SA automatic gas adsorption device. Before characterization measurements were performed, the samples were out gassed in vacuum at 150 °C. Two different amounts of each oxide were examined and BET method was applied on the results to calculate a BET surface area.

Catalytic activity of the samples was measured under an atmospheric pressure using a flow reactor device. There was a 50 mg of sample inserted between two 50 mg pieces of silica-wool into a pyrex U-shaped tube (1 cm in diameter, 45 cm in length). The tube was placed in a cylindrical-shaped furnace. Gas was composed of 10% CO, 10% O₂ and 80% He, the total flow rate of 20 ccm/min. was controlled by flowmeters. Composition of the output gas was analyzed using a quadrupole mass spectrometer STANDAM ST-200P located in a capillar-connected high vacuum chamber. Masses corresponding to He, H₂O, CO, O₂ and CO₂ were recorded at intervals of 1 s. The temperature has been controlled and recorded using two thermocouples located close to the sample, outside of the pyrex tube. Two sequential cycles of gradual annealing up to 320 °C and cooling down to room temperature (24 hours each) were

applied on each sample and one to each oxide support. There was also examined a catalytic activity of used silica-wool and it proved negligible.

TEM images were obtained with a JEOL JEM2000-EX transmission electron microscope operating at 200 kV, using carbon covered Cu grid. SEM observation were carried out with a HITACHI S-5000 scanning electron microscope operating at 10 kV. Ultrasonic pretreatment in ethanol was applied on each sample before TEM and SEM observations.

3. RESULTS AND DISCUSSION

3.1 Characterization of structural properties

Oxide supports were analyzed by BET method and following BET surface areas were determined: 10 m²/g for ZnO, 15 m²/g for CeO₂ #3 and 12 m²/g for CeO₂ #4.

Prepared CeO₂ #3 and #4 before and after calcination and oxides loaded with metal as prepared, after reduction and after CO oxidation in flow reactor were observed using a high resolution TEM and SEM techniques.

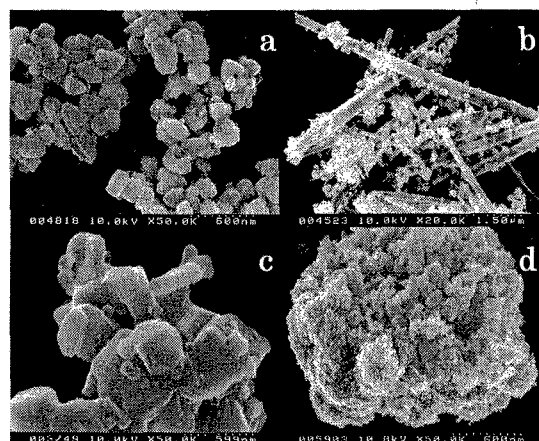


Fig. 1. SEM images of CeO₂ #4 as prepared (a), CeO₂ #3 after calcination (b), PdGa/ZnO (3 wt.% Pd, 2.3 wt.% Ga) as prepared (c) and Pd/CeO₂ #3 (13.9 wt.% Pd) after treatment in flow reactor (d).

In the Fig. 1(a) one can see as prepared CeO₂ #4. There are oxide particles of two sizes present, smaller of 40 nm mean size in a diameter and larger of 160 nm mean diameter. CeO₂ #3 has got similar structure after preparation and also particles are of the same mean size as #4. But after calcination there is no significant difference of the structure of CeO₂ #4, while CeO₂ #3 is composed of nanotubes and small particles (see Fig. 1b). This indicates that the properties of CeO₂ toward catalysis can be enhanced by change of calcination conditions. Different calcination should be applied on the same oxide in the future in order to observe its catalysis.

After loading the CeO₂ support with Pd, we can see small nanoparticles most probably composed of Pd (Fig. 2b), as well as large agglomerates of Pd and oxide particles (Fig. 2a).

Pd forms small nanoparticles of several nanometers in size or small clusters on a ZnO. PdGa loaded ZnO is of similar structure (Fig. 1c, 2c). No significant changes of the metal deposit occurred after reduction of the samples. The knowledge of Pd and Ga distribution in the clusters is important for understanding the processes proceeding on a surface during catalytic CO oxidation, therefore we

need an elemental mapping observation in the future.

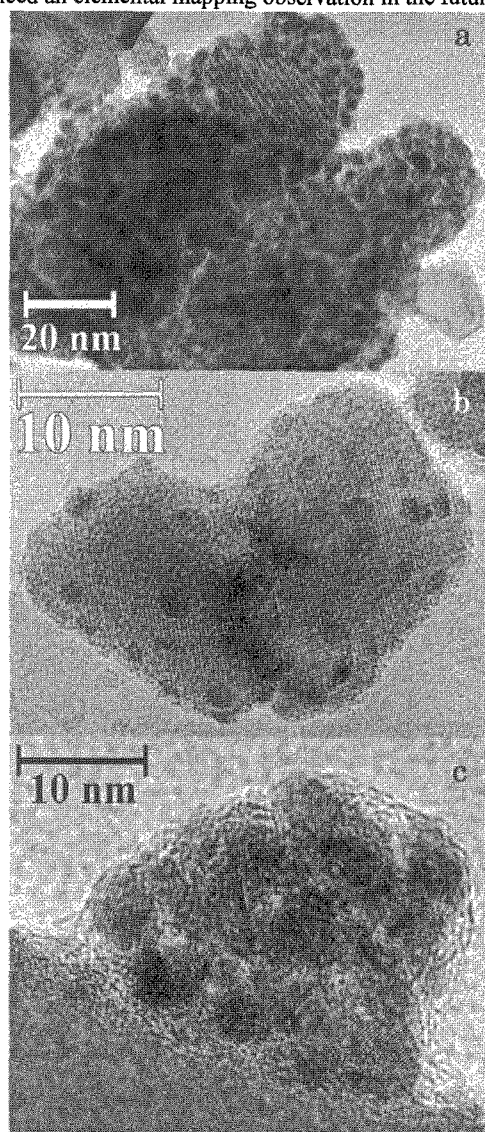


Fig. 2. TEM images of Pd/CeO₂ #2 as prepared (a), Pd/CeO₂ #2 after reduction (b) and PdGa (4.8 wt.% Pd, 1.6 wt.% Ga) as prepared (c).

A thin layer was observed by TEM all over the surface of Ga loaded CeO₂ #3, which was not recognized in the case of Pd loaded samples. Possibly, this can be a film of carbon evaporated from the grid, but more probably it is a layer of Ga. It is also corresponding to following CO oxidation results.

After treatment in a flow reactor all CeO₂ supported samples exhibit formation of large clusters, up to 1 μ m in size (Fig. 1d).

We can conclude that Pd loaded on various CeO₂ forms agglomerates. This is decreasing a surface area of both oxide and Pd. On the other hand, Pd or PdGa are distributed more effectively on the surface of ZnO and forms well defined structure of nanoparticles, which is also good for theoretical studies of heterogeneous catalysis.

3.2 CO oxidation activity

Catalytic properties of prepared samples have been

examined using a flow reactor. There was a different behavior observed during first and following annealing cycles. Two annealing cycles have been investigated due to this activation process. Starting temperature of CO oxidation (when CO₂ intensity reaches its maximum) can be found in the Table I. for each sample.

Usually, present CO was not completely converted, but experiments performed with two similar samples of different weight showed that the CO conversion rate is slightly increasing when we use larger amount of the sample. CO conversion rates are in the Table I.

Catalytic CO oxidation is endothermic reaction. Therefore the temperature of reaction die out can be lower compared to temperature at which it started, because the sample is heating itself when reaction is proceeding. This effect was observed, but cannot be discussed quantitatively, because the thermocouple was placed outside of the pyrex tube. Therefore the measured temperature may slightly differ from the actual temperature of the sample.

It the Fig. 3, one can see reaction curves obtained in-process of first annealing of the oxide supports with no loading. Unfortunately there was not possible to measure activity of CeO₂ #1 and #2 samples.

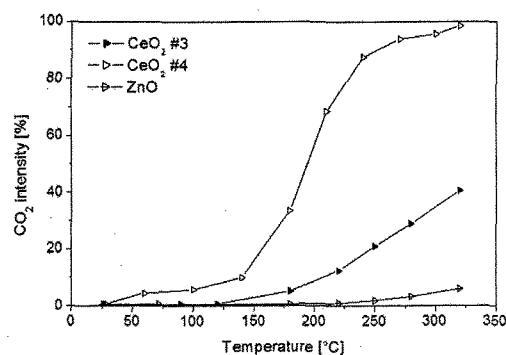


Fig. 3. Standardized CO₂ intensity measured on oxides during first annealing in a flow reactor (100% is a CO₂ maximum intensity reached in all the experiments).

Appreciating the oxides in light of catalytic properties, samples CeO₂ #2 and #4 seems to be the best support for palladium nanoparticles.

When analyzing recorded flow reactor data, we can observe similar behavior in the case of samples loaded only with Pd. CO₂ intensity is at first gradually increasing with increasing temperature. This increase is always correspondent to observed CO oxidation ability (Fig. 4) of used oxide substrate. Thereafter, a big jump of CO₂ intensity up to maximum value occurs, which must be caused by activity of Pd. This indicates that CO oxidation properties of impregnated Pd and oxide substrate are of additive character and doesn't influence each other.

There is no evidence of catalytic activity in the case of all of the Ga only loaded samples and moreover the activity of oxide support is repressed by Ga. This confirms the above mentioned thesis, that Ga forms a thin layer on the surface of oxide, as observed by TEM.

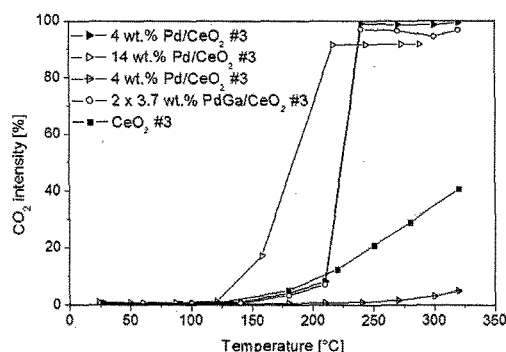


Fig. 4. Standardized CO₂ intensity measured on oxides during first annealing in a flow reactor (100% is a CO₂ maximum intensity reached in all the experiments).

When we deposit Pd and Ga together on an oxide substrate, the catalytic activity of oxide is repressed by Ga. The activity of Pd stays unchanged when increasing a temperature and a difference occurs by temperature decrease, compared to correspondent sample loaded only with Pd. The oxidation reaction is progressing longer and dies out at the lower temperature. Comparing Pd and PdGa loaded samples there is a difference of 20 °C on CeO₂ #3 support and 20 °C (3 wt.% Pd, 2.3 wt.% Ga) and 50 °C (4.8 wt.% Pd, 1.6 wt.% Ga) in case of ZnO support. This effect is increasing with decreasing concentration of Ga and takes affect during the second annealing cycle. This indicates some activation process during the first cycle of annealing which cannot be uncovered using available results.

We can only guess that this influence of Ga is only of morphology origin. It doesn't provide us any evidence of bimetallic interaction between Pd and Ga.

Also influence of amount of loaded Pd was studied. In the Table I we can see that the temperature of catalytic CO oxidation generally decreases with increasing Pd weight concentration.

Sample composed of 9.5 wt.% of Pd loaded on ZnO endured a catalytic properties stability test. After more than 120 hours in a flow reactor at 250 °C, there was no decrease of CO oxidation ability observed and 0.25 m³/g of CO were converted (standatized on sample weight) with 92 % conversion rate.

4. CONCLUSIONS

It was found that CO oxidation properties of impregnated Pd and oxide substrate are of additive character and doesn't influence each other. Whereas Ga deposited on oxides has no CO oxidation ability and moreover it is repressing the catalytic ability of the oxide substrate. However Ga deposited altogether with Pd doesn't influence the activity of Pd and it helps to keep the oxidation reaction progressing longer during the temperature decrease. Mentioned properties are not dependent on a type of used oxide.

Metals loaded on various CeO₂ forms agglomerates which is decreasing a surface area of both the oxide substrate and loaded metal. Deposited metals are distributed more effectively on ZnO and forms well defined and stationary structure. CeO₂ seems to be better substrate for CO oxidation than ZnO because of its good

catalytic properties, but its preparation conditions must be improved in order to increase a surface area. Also effect of agglomeration after deposition of metals must be eliminated.

Catalysts selectivity, which is very important for fuel cells application, was not part of this study. Interaction of prepared catalysts with H₂ and CH₄ is an object of further research.

Also influence of Pd amount, CO concentration and reduction conditions is to be focused in further studies and catalytic reaction stability test is to be performed on more of the prepared samples in the future.

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