EFFECT OF CERIA AND ZIRCONIA ON THE ACTIVITY OF Pd ONLY THREE WAY CATALYST

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Abstract

Mixed ZrO₂-CeO₂ oxides were studied as a carrier of Pd catalysts for combustion of oxygenated compounds. The effect of support composition on catalytic oxidation of ethanol on Pd/ZrO₂-CeO₂ catalyst was investigated. Prepared Zr-Ce mixed oxides with different composition were added to aluminium hydroxide and used for washcoating of ceramic monolithic carriers. Performance of Pd catalysts supported on these monoliths for reduction of NO and oxidation of CO in real exhaust gasses from gasoline fueled engine was studied. Activity of the elaborated monolithic catalysts was compared with activity of commercial three way catalyst. It was stated that composition of support affects on the activity of Pd/ZrO₂-CeO₂ catalysts in catalytic oxidation of ethanol (and on the distribution of the reaction products) as well as on the activity in oxidation CO and reduction NO over monolithic Pd only catalysts.

1. Introduction

Extensive researches are focused on the replacement of Rh in three-way catalyst (TWC). Rhodium that is a key component of these catalysts responsible for NOx reduction, is also the most expensive one. Palladium has been considered as an alternative for Pt-Rh system however Pd-based systems still need improvement [1, 2]. It has been often demonstrated that the effects of the carrier on the metal catalysts performance can be significant. Modification of the composition of alumina support by addition of different metal oxides (especially ceria) is regarded as a method of performance enhancement of catalysts for treatment of automotive exhaust gasses [3]. It seems, that promotion by ceria can be extended to other oxides to maintain or even increase the durability of the TWC while decreasing emissions, especially during cold-start. In particular, Zr-Ce mixed oxides seem to be attractive because ZrO₂ related materials have found wide utility in catalysis due to unique surface properties. Mixed ZrO₂-CeO₂ oxides are regarded as a important additives or promoters in automotive catalysts. Introduction of zirconia in to a solid solution with ceria improves both the bulk mobility of oxygen and catalyst thermal stability as well as increases the number of surface anionic vacancies [4 - 6]. On the other hand it was also reported that ceria-zirconia on alumina shows inferior catalytic performance than ceria promoted catalyst [7].

Ethanol and MTBE are commonly used as a fuel additives. Vehicle tests have demonstrated that these components lower emissions of hydrocarbons and CO. However it also appeared that exhaust gasses contain notably amounts of unburned alcohol and other species like aldehydes when gasoline containing oxygenates is used. Formaldehyde (acetaldehyde) and unburned alcohols are serious toxic air pollutants due to potential health effects and photochemical reactivity.
The presented work was undertaken for investigation of the effects of Zr-Ce mixed oxides on the efficiency of Pd catalyst in ethanol combustion (and its selectivity in formation of acetaldehyde) as well as on the performance of Pd-based TWC. The study presents results of the ethanol oxidation over palladium catalysts on carrier consisting of co-precipitated zirconiia-certa with different composition. Prepared ZrO₂-CeO₂ materials were also applied for preparation of washcoats for Pd-only TWC. Effect of the washcoat composition on the activity of these catalysts in oxidation of CO and reduction of NO from real exhaust gasses was investigated.

2. Experimental

Mixed ZrO₂-CeO₂ oxides with atomic ratio Zr:Ce equal 0:1; 1:4; 1:1; 4:1 and 1:1 were prepared by co-precipitation from solution of zirconyl chloride and cerium nitrate of the appropriate concentration. The hydroxide precursor was precipitated by simultaneous addition of corresponding solution and ammonia into water, keeping pH between 9 – 9.5. The precipitates were filtered, dried at 383 K for 24 h and calcined for 4 h at 873 K. After that materials were milled and used for supporting of Pd catalyst or for washcoats preparation.

*Table 1. Specific surface area of the prepared Zr-Ce oxides and symbols of related monolithic catalysts*

<table>
<thead>
<tr>
<th>Zr:Ce ratio</th>
<th>Surface area, m²/g</th>
<th>Monolithic catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>0:1</td>
<td>38</td>
<td>C1</td>
</tr>
<tr>
<td>1:4</td>
<td>43</td>
<td>C2</td>
</tr>
<tr>
<td>1:1</td>
<td>66</td>
<td>C3</td>
</tr>
<tr>
<td>4:1</td>
<td>70</td>
<td>C4</td>
</tr>
<tr>
<td>1:0</td>
<td>62</td>
<td>C5</td>
</tr>
</tbody>
</table>

0.1 wt% of Pd was supported on the calcined Zr-Ce oxides by impregnation with solution of PdCl₂. Catalytic activity in combustion of ethanol and selectivity to acetaldehyde (ACA) of the resulted catalysts was then determined. Tests were performed in a flow apparatus, which consist of feed unit, reactor and on-line gas chromatograph (FID). The experimental conditions: the catalyst weight = 100 mg diluted with SiC to 1 cm³ of volume bed, GHHSV = 15000 h⁻¹. The feed composition: 8.4 %vol. of O₂ in nitrogen, molar ratio ethanol:O₂ = 1:10. The reaction products were analyzed by on-line GC. Ethanol conversion and reaction products composition were measured as a function of temperature. Before test the catalysts were reduced under hydrogen flow at 673 K for 1 h.

Prepared materials were characterized by DRON-3 X-ray diffractometer. The surface area was determined by the BET, from nitrogen adsorption data obtained using Sorptomatic 1900 Fisons instrument. XRD patterns are shown in Fig. 2. Specific surface area of the prepared Zr-Ce carriers is presented in the Table 1.

30wt.% of the milled ZrO₂-CeO₂ material was mixed with DISPERAL aluminum hydroxide and the mixture was suspended in acidified water medium. Obtained slurry obtained was used for washcoating of monoliths (cordierite honeycomb support: d = 102 mm, h = 98 mm, 400 cup supplied by CORNING); monolith was immersed in the suspension for ca 5 min. then it was removed and an excess of slurry was blown out. After drying and calcination (2 h at 823 K) this procedure was repeated until loading of ca. 150 g of Al₂O₃-(ZrO₂-CeO₂)/dm³ was achieved. Finally washcoated monoliths were impregnated by dip-coating with acidified solution of palladium chloride, dried and calcined. The final Pd loading was 4 g/dm³.
Performance of monolithic palladium catalysts for reduction of NO and oxidation CO was studied under real exhaust gas conditions. The engine performance tests were conducted on dynamometer equipped engine (Fiat Seicento, 899 cm$^3$) fueled with gasoline. Monolithic catalysts were canned in a stainless steel cylinder and connected to exhaust system of engine. A flow sheet of the experimental set-up is given in Fig. 1. In the static test the engine was operated at a constant lambda value. Temperature of the exhaust gasses was controlled by the engine loading.

<table>
<thead>
<tr>
<th>Engine speed, min$^{-1}$</th>
<th>GHSV, h$^{-1}$</th>
<th>Catalyst temperature, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>45 000</td>
<td>628 – 758</td>
</tr>
<tr>
<td>3000</td>
<td>67 500</td>
<td>643 – 847</td>
</tr>
<tr>
<td>4000</td>
<td>90 000</td>
<td>798 – 883</td>
</tr>
</tbody>
</table>

After stabilization of the engine, the concentration of CO and NO in exhaust gas was measured and then engine speed was increased to the next set. Composition of exhaust gasses, before and after the catalytic converter, was analyzed by use of URAS 10E apparatus. The fresh catalyst was conditioned at $\lambda = 1 \pm 2\%$ for 1 h. Activity of the prepared catalyst was compared with the activity of the commercial TWC.

3. Results and discussion

The XRD patterns of some prepared mixed Zr-Ce oxides are shown in Fig. 2. The XRD spectrum of these materials show sharp and intense peaks corresponding to solid solutions of CeO$_2$-ZrO$_2$. Some inhomogeneity (clusters of c- and t-CeO$_2$) is visible. Cells parameters can be related with formal composition of the mixed Zr-Ce oxide.

Composition and specific surface area of the investigated ZrO$_2$-CeO$_2$ mixed oxides are presented in the Table 1. It is seen that prepared materials present quite high specific surface area. Bare zirconia (Zr:Ce = 1:0) exhibits distinctly higher surface area than bare ceria (Zr:Ce
Mixed oxides described by the value of Zr:Ce ratio equal 1:1 and 4:1 possess somewhat higher specific surface areas than both pure components — zirconia and ceria.

![Graph](image)

*Fig. 2. XRD patterns of mixed Zr-Ce oxides.*

Combustion of ethanol over examined palladium based catalysts causes its both total (to CO₂) and partial oxidation (to ACA and others organic products). Different amounts of diethyl ether, acetic acid, ethyl acetate and other compounds were registered in the reaction products however acetaldehyde was the major organic product of ethanol oxidation. The most important feature of catalysts used for this type of pollution control is selectivity towards complete ethanol combustion.

Figure 3 shows the total conversion of ethanol over Pd/ZrO₂-CeO₂ catalysts as a function of reaction temperature. One can say that prepared Pd catalysts distinctly differ in the activity, the highest conversion of ethanol was found over that one supported on zirconia (Zr:Ce = 1:0), the lowest activity exhibits catalyst supported on ceria (Zr:Ce = 0:1). Catalysts supported on mixed Zr-Ce carriers show intermediate activity. The light-off temperatures (temperature at which 50% conversion of ethanol is obtained) for the examined catalysts increase in the following order of catalyst carriers: Zr:Ce = 1:0 < 1:1 < 4:1 < 1:4 < 0:1. Corresponding temperatures for 50% of ethanol conversion are respectively: 416 K; 426 K; 430 K; 444 K and 456 K. Higher activity of the zirconia supported catalyst in comparison to ceria supported one can be related with distinctly larger surface are of this carrier.

![Graph](image)

*Fig. 3. Conversion of ethanol over Pd catalyst supported on investigated carriers as a function of reaction temperature.*

![Graph](image)

*Fig. 4. Selectivity to ACA over Pd catalyst supported on investigated carriers as a function of reaction temperature.*
Acetaldehyde is the main carbon containing organic product of ethanol oxidation over catalysts examined in the work. The selectivity to ACA over investigated catalysts varies widely as it is shown in Fig. 4. The highest selectivity shows catalyst supported on pure zirconia (Zr:Ce = 1:0), the lowest exhibit catalysts supported on mixed ceria-zirconia carriers characterized by Zr:Ce ratio = 1:4 and 1:1. For all of examined catalysts the maximum of the selectivity to ACA reaches a maximum at ca 470 K and then, for the catalysts supported on either pure zirconia or ceria, decreases sharply at higher temperatures. Catalysts supported on mixed Zr-Ce materials show slightly lower selectivity than those ones prepared on either pure zirconia or ceria.

![Graphs showing conversion of CO and reduction of NO over catalysts](image)

Fig. 5. Conversion of CO over monolithic catalysts as a function of exhaust gases temperature. Engine speed: 2000min⁻¹.

Fig. 6. Reduction of NO over monolithic catalysts as a function of exhaust gases temperature. Engine speed: 2000min⁻¹.

The experiments of ethanol combustion show that composition of the carrier affects on the activity of Pd catalyst in conversion of this molecule. Prepared catalysts exhibit quite high activity for this reaction at low temperature. However combustion of ethanol is not complete and by-products are formed. The lowest amounts of by products were formed on the catalysts supported on mixed ceria-zirconia carrier. Selectivity to ACA over Pd catalysts supported on the investigated carriers increases in the following order (described by Zr:Ce ratio): 1:4 – 1:1 < 4:1 < 0:1 < 1:0.

The designed Pd only monolithic catalysts supported on alumina-ceria-zirconia washcoat were evaluated in the treatment of real engine exhaust stream. The results of these tests are presented in Figs. 5 - 10. On the basis of the presented results the influence of the Zr:Ce ratio on the oxidation of CO and reduction of NO can be evaluated.

![Graphs showing conversion of CO and reduction of NO over catalysts](image)

Fig. 7. Conversion of CO over monolithic catalysts as a function of exhaust gases temperature. Engine speed: 3000min⁻¹.

Fig. 8. Reduction of NO over monolithic catalysts as a function of exhaust gases temperature. Engine speed: 3000min⁻¹.

292
The performance of the elaborated catalysts was compared with that of a reference (commercial) TWC. The observed differences in oxidation of CO for the examined catalysts depend on the composition of the mixed Zr-Ce oxide added to alumina washcoat. In spite of the lack of platinum prepared catalysts gave relatively high conversion of CO. The highest conversion of CO was found for the C3 and C2 catalysts supported on the washcoat modified by addition of respectively Zr:Ce = 1:1 and 1:4 mixed Zr-Ce oxides. Comparing activity of these catalysts with activity of commercial one only small differences in CO conversion can be stated.

Prepared monolithic catalysts exhibit lower activity in NO reduction than commercial one. However the for the C3 catalyst containing (Zr:Ce = 1:1) mixed ceria-zirconia, quite high level of NO reduction was observed. It is worth to notice that this catalyst shows also high activity in CO conversion. On the other hand in the test of ethanol combustion the Pd catalyst supported on (Zr:Ce = 1:1) mixed zirconia-ceria carrier, exhibits high conversion of ethanol and low selectivity to ACO. In this way it can be supposed that addition of ceria-zirconia mixed oxide (with composition Zr:Ce = 1:1) to the washcoat of monolithic Pd catalyst, would improves its efficiency in the treatment of exhaust gasses from engine fueled with gasoline containing ethanol.

![Fig. 9. Conversion of CO over monolithic catalysts as a function of exhaust gasses temperature. Engine speed: 4000 min⁻¹.](image1)

![Fig. 10. Reduction of NO over monolithic catalysts as a function of exhaust gasses temperature. Engine speed: 4000 min⁻¹.](image2)

The results of the engine tests confirm, that addition of the mixed ZrO₂-CeO₂ mixed oxide (Zr:Ce = 1:1) to the alumina based washcoat enable one to prepare monolithic Pd only catalyst that presents high activity (comparable with that of commercial TWC) in oxidation of CO conversion and reduction of NO from real exhaust gasses.

4. Conclusions

The choice of the optimal catalyst for vehicles fueled with gasoline containing ethanol is a question of the selection of the active material that produces the smallest amount of products of ethanol partial oxidation and in the same time exhibits high activity in CO and NO conversion.

Results of this work show that addition of ceria-zirconia to alumina support affects composition of the products of ethanol oxidation at low temperature. The most important by-product is acetaldehyde.

The conversion of ethanol over palladium catalyst supported on the mixed ZrO₂-CeO₂ is significantly altered by composition of this carrier. The following order of catalytic activity in ethanol conversion was observed: Zr:Ce = 1:0 > 1:1 ~ 4:1 > 1:4 > 0:1. The lowest
selectivity to acetaldehyde was observed over Pd catalysts supported on mixed Zr-Ce oxides characterized by the Zr:Ce ratio = 4:1 and 0:1.

Under conditions of engine test, the monolithic Pd catalyst supported on washcoat composed of alumina and 30% wt. of ZrO₂-CeO₂ (Zr:Ce = 1:1) exhibits high activity (comparable with activity of commercial catalyst) in CO and NO conversion contained in real exhaust gasses.

Acknowledgements

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References