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Partial oxidation of methanol over Au/CeO$_2$-ZrO$_2$ and Au/CeO$_2$-ZrO$_2$-TiO$_2$ Catalysts

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Experimental data on hydrogen production via partial oxidation of methanol (POM) reaction on Au/ZrO$_2$, Au/CeO$_2$-ZrO$_2$ and Au/CeO$_2$-ZrO$_2$-TiO$_2$ catalysts is presented in this article. Gold catalysts were prepared by deposition-precipitation (DP) method and characterized by XRF, XRD, H$_2$-TPR, XPS methods $N_2$ adsorption. The activity results show that catalyst containing 1 % wt. gold supported on CeO$_2$-ZrO$_2$ carrier demonstrates very good hydrogen selectivity and the highest catalytic activity among all tested catalysts. The optimal working temperature established was 375°C. At this temperature 75.5% hydrogen selectivity was registered. The presence of oxidized gold in the catalyst’s composition as well as the support redox properties are the major factors controlling the observed catalytic activity.

Introduction

Partial oxidation of methanol (POM) is an exothermic reaction and does not need the addition of steam in the reaction mixture [1]. It is thermodynamically favourable at mild reaction condition. In contrast, methanol steam reforming is an endothermic reaction and needs addition in situ steam, which requires extra energy consumption.

Gold-based catalysts are known for their superior activity for low-temperature CO oxidation, WGSR as well as number of organic compounds [2–5]. Some of the published reports show that gold catalysts are also active for methanol partial oxidation demonstrating low selectivity towards CO formation and high selectivity towards hydrogen production.

For example, POM carried out in the presence of gold promoted copper-zinc oxide catalyst was reported to show 97 % of hydrogen selectivity and 5.5 % of CO selectivity at 190 °C[6].

The oxidation activity of gold catalysts strongly depends upon the size of gold nanoparticles and on the ability of support to provide during the reaction the active oxygen species [7].

Gold catalysts supported on reducible metal oxides are much more active in CO oxidation than the gold catalysts supported on non-reducible oxides, for example Au/TiO$_2$ and Au/Fe$_2$O$_3$ are much more active than the Au/Al$_2$O$_3$ [8].

CeO$_2$ has been successfully used by many researchers as a support for gold catalysts in different oxidation reactions, because it possesses several advantageous properties like high oxygen storage capacity, good redox properties, ability to release the storage oxygen during the reaction at low temperatures [9].

ZrO$_2$ is another attractive support material because of its stability at high temperatures and suitable mechanical and chemical properties. Researchers have proved that the addition of zirconia to the ceria leads to the formation of mixed oxides with increased thermal stability and optimal redox property compared to the single cerium or zirconium oxides [10, 11]. Mixed cerium - zirconium oxide supports forms smaller crystallites than the single oxides.

By supporting of both Au and Cu on CeO$_2$-ZrO$_2$ carriers catalysts for steam reforming of methanol with good catalytic activity and low CO selectivity at mild reaction temperatures has been prepared [10, 12].

In this work, results of studies of the catalytic properties of (mechanically mixed oxide CeO$_2$-ZrO$_2$ oxide systems) and gold containing catalysts Au/ZrO$_2$, Au/ (mechanical mixture of CeO$_2$-ZrO$_2$) and Au/ (mechanical mixture of CeO$_2$-ZrO$_2$-TiO$_2$) in POM reaction have been studied. An attempt for revealing the relation between the catalytic performance of the gold catalysts and their compositions and structures is proposed.

Experimental

Catalyst preparation

The deposition-precipitation of gold on mixed oxide supports was carried out in a Mettler Toledo Labmax reactor, which permits the precise control of the pH, temperature, liquid reagent delivery rates and mixing of the suspension. The CeO$_2$-ZrO$_2$-TiO$_2$ and CeO$_2$-ZrO$_2$ supports were prepared by simple mechanical mixing of the components. The needed amounts of CeO$_2$ (Acros Organics), ZrO$_2$ (Aldrich Chemistry) and TiO$_2$ (Sigma-Aldrich) were correctly measured and ultrasonically mixed for 1 h, then dried in the oven at 120 °C for 3 h prior to the gold deposition. In gold deposition experiments, the total gold loading was fixed at 1 wt. %. A 0.1 M
solution of KOH and de-ionized water were filled in the reactor to reach the pH = 12.7 at intensive mixing, and then the liquid was heated to 60 °C. After reaching the desired temperature and pH, heated to 60 °C support and exact amount of aqueous solution of HAuCl₄·3H₂O (Sigma-Aldrich) precursor were added to the reactor at intensive mixing. After that within 5 min pH was adjusted to 10.4 by addition of 0.5 M of HNO₃, then pH was adjusted to 8 by the addition of 0.1 M of HNO₃ in the next 5 min. Then the suspension was aged at 60 °C for 1 h at intensive mixing. The pH tuning was done by adding specified amounts of the Mg-citrate solution. Then the suspension was filtered and the obtained solid was washed with hot de-ionized water several times until chloride ions were totally removed. Removal of chloride ions was confirmed by addition of the drops of AgNO₃ solution to the washing waters. Then the prepared catalytic mass was dried overnight at 100 °C and calcined at 500 °C for 5 h in air. After calcination the sample was pelletized, grounded and a fraction of particles size between 0.01-0.03 mm was separated. This fraction was used for further activity tests and catalyst characterizations.

**Catalytic activity measurements**

The catalytic activity experiments were carried out in a (PID Eng & Tech, system, Spain) with a fixed bed quartz reactor (o.d. = 6 mm). The experimental setup is shown in Fig. 1. Experiments were carried out at atmospheric pressure and temperatures in the interval from 275 to 450 °C. The reactor was located in a temperature programmable furnace with a K type thermocouple placed in the centre of the catalyst bed. For each experiment, the reactor was charged with 0.100 g of catalyst sample. Before the reaction, the gold catalysts were oxidized by helium-oxygen mixture (20 % volume oxygen) with total flow 40 cm³ min⁻¹ at 500 °C for 12 h. Then reactor temperature was decreased to 120 °C, and the reaction mixture was introduced in to the reactor. The total flow was kept at 50 cm³ min⁻¹ with an O₂:CH₃OH molar feed ratio 0.5. Methanol was delivered by Bronkhorst High-Tech B.V. controlled evaporation mixing (CEM) liquid delivery system, which incorporates a readout/control unit. This unit can precisely control the liquid/gas mixture and has very stable vapor flow rate reproducibility. At room temperature, methanol liquid is drawn from container with a N₂ gas blanket at differential pressure of 4 bar. The methanol liquid was measured by a micro flow type liquid mass flow controller. 0.52 cm³ h⁻¹ of methanol gas flow is established by a control valve that forms an integral part of the CEM system. The liquid (methanol) and 20 cm³ min⁻¹ of helium carrier gas were mixed in a mixing chamber, and subsequently led into the temperature controlled heat exchanger and then to the reactor unit. The reactants and reaction products were periodically analysed using an intermittently connected Micro GC 490 with Molecular sieve-5A and CP-Sil 5CB channel. Three analyses of reaction products were recorded for each reaction condition to monitor the repeatability of the experimental measurements. In addition, all of the catalysts were used twice to check the reproducibility. The results were highly reproducible (with standard variance ±1) under the set parameters of the PID Microactivity apparatus. This result means that prepared catalysts have very heterogeneous structure and composition. The measurements were carried out when the reaction reached steady state (after 75 minutes for each set of reaction conditions). Methanol conversion (in mol %), hydrogen selectivity (%) and CO selectivity (%) were calculated according to the following formulas (1) – (3).

\[
\text{CH}_3\text{OH conversion} (\%) = \left( \frac{\text{moles of CH}_3\text{OH in}}{-\text{moles of CH}_3\text{OH consumed}} \right) \times 100
\]

\[
\text{H}_2\text{selectivity} (\%) = \left( \frac{\text{moles of H}_2 \text{ produced}}{-\text{moles of CH}_3\text{OH consumed}} \right) \times 100
\]

\[
\text{CO selectivity} (\%) = \left( \frac{\text{moles of CO produced}}{-\text{moles of CH}_3\text{OH consumed}} \right) \times 100
\]

**Catalysts characterization**

The surface area of the prepared catalysts and supports were determined by measuring the nitrogen adsorption/desorption isotherm using NOVA (2200e) High Speed Surface Area and Pore Size Analyzer (Quantachrom, USA). Before each experiment, the samples were degassed at 300 °C for 3 h in order to remove adsorbed water and impurities.

X-ray Fluorescence (XRF) analysis was carried out using AMPTEK XRF Kit in Equinox 1000 (France) system. Silver X-ray source was used, and operated at 100 KV and 30 mA. X-ray powder diffraction (XRD) patterns were using INEL CPS 180 powder diffractometer Equinox 1000 (France) system operated at 40 KV and 30 mA using Co-Kα1 radiation (λ=1.789 Å), from 0 to 120 °. Exposure time was 7200 s, with a flat radiation sample holder.

![Schematic diagram for partial oxidation of methanol reaction system](image-url)
Temperature programmed reduction (TPR) experiments were conducted on ChemBet PULSAR TPR/TPD automatic chemisorption analyzer (Quantachrom, USA). The catalyst samples were placed in a U-shaped quartz sample cell, located in a furnace controlled by programmable heating system. In each experiment, 200 mg of the catalyst was preheated under the He flow of 80 cm$^3$ min$^{-1}$ at 120 °C for 45 min. Then the temperature was decreased to 40 °C, and a reducing gas mixture (5 % H$_2$ and 95 % N$_2$) was introduced at a flow rate of 15 cm$^3$ min$^{-1}$. The temperature was increased from 40 to 700 °C by ramping rate of 5 °C min$^{-1}$. Consumed hydrogen amount was determined by thermal conductivity detector (TCD).

The X-ray Photoelectron Spectroscopy (XPS) measurements were carried out in an ultrahigh vacuum multi technique surface analysis system (SPEC GmbH, Germany). A standard dual anode X-ray source SPECS XR-50 with Mg-Kα, 1283.6 eV was used to irradiate sample surface with 13.5 KV, 100 W X-ray power and a take-off-angle for electrons at 90° relative to sample surface plane. The irradiate sample surface with 13.5 KV, 100 W X-ray power and a take-off-angle for electrons at 90° relative to sample surface plane. The sample was pressed into pellets and transferred into the test chamber. The analysis chamber was maintained at 5.10$^{-8}$ bar during all measurements. As the standard practice in XPS studies, the surface oxygen. The origin of this spectrum can be connected with gold nanoparticles. This peak might be attributed to the reduction of oxygen species' surrounding the gold nanoparticles. H$_2$ consumption during the samples reduction had been investigated by TPR studies. Fig.3 shows H$_2$-TPR profiles for CeO$_2$-ZrO$_2$ support and for Au/ZrO$_2$, Au/CeO$_2$/ZrO$_2$ and Au/CeO$_2$/ZrO$_2$-TiO$_2$ catalysts.

(i) The TPR spectrum of CeO$_2$/ZrO$_2$ support (Fig.3a) has only one reduction peak at 552 °C that represents the reduction of the CeO$_2$ surface oxygen.

(ii) In the TPR spectrum of Au/ZrO$_2$ catalyst (Fig 3.b) a very broad and low intensity reduction peak was registered between 295 to 370 °C. This peak might be attributed to the reduction of oxygen species' surrounding the gold nanoparticles.

(iii) In the TPR spectrum of Au/CeO$_2$/ZrO$_2$ catalyst (Figure 3.d) one complex reduction peak was observed with maximum at temperature of 184.2 °C, formed by overlapping of several peaks. The origin of this spectrum can be connected with gold particles reduction process. It is well known that the small metal particles are reduced at lower-temperatures than the larger particles [12]. Therefore, the overlapping peaks represent the consecutive reduction of narrow groups of gold particles with nearly equal average particles size. This is also an indication that average particles size of gold particles has narrow distribution.

(iv) In the TPR spectrum of Au/CeO$_2$/ZrO$_2$-TiO$_2$ sample, (Fig. 3c) the similar reduction behaviour is observed. The gold particles reduction peaks are shifted slightly toward higher temperatures. This is indication that average gold particles in Au/CeO$_2$/ZrO$_2$ are smaller than in the Au/CeO$_2$/ZrO$_2$-TiO$_2$ catalyst.

**Results and Discussion**

**Catalyst characterization**

The chemical and physical properties of CeO$_2$/ZrO$_2$, Au/ZrO$_2$, Au/CeO$_2$/ZrO$_2$ and Au/CeO$_2$/ZrO$_2$-TiO$_2$ catalysts are summarized in Table 1. BET results shows that, three catalysts and CeO$_2$/ZrO$_2$ support have almost same surface area. 

The results of the XRF elemental analysis shows that above 0.90 % of the gold introduced in the process of catalyst preparation were successfully deposited on the support. Therefore, it proves that gold deposition was done properly.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET Surface area (m$^2$/g)$^a$</th>
<th>Au particles size$^b$ nm</th>
<th>Catalysts composition from XRF$^b$ (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$/ZrO$_2$</td>
<td>118.0</td>
<td>-</td>
<td>Au 75.02, CeO$_2$ 24.98, ZrO$_2$ 2.00</td>
</tr>
<tr>
<td>Au/ZrO$_2$</td>
<td>117.0</td>
<td>4.92, 0.96</td>
<td>Au 100.04, CeO$_2$ 0.00, ZrO$_2$ 0.00</td>
</tr>
<tr>
<td>Au/CeO$_2$/ZrO$_2$</td>
<td>120.1</td>
<td>4.13, 0.90</td>
<td>Au 24.56, CeO$_2$ 75.54, ZrO$_2$ 0.00</td>
</tr>
<tr>
<td>Au/CeO$_2$/ZrO$_2$-TiO$_2$</td>
<td>112.0</td>
<td>3.16, 0.99</td>
<td>Au 24.99, CeO$_2$ 54.91, ZrO$_2$ 20.90</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>a</th>
<th>BET surface area from N$_2$ adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
<td>Chemical composition analysis result from XRF</td>
</tr>
<tr>
<td>c</td>
<td>From TEM measurements (Also supplementary Fig. S1)</td>
</tr>
</tbody>
</table>
The presence of Au strongly depresses the reducibility of the catalyst's oxide support. The reduction peak detected in TPR spectrum of CeO$_2$-ZrO$_2$ sample at 552 °C was not detected in the TPR spectra of Au containing samples. This means that presence of gold in the catalyst composition is strongly depressing the oxygen mobility in CeO$_2$-ZrO$_2$ and CeO$_2$-ZrO$_2$-TiO$_2$ mixed oxide systems. Therefore, the reducibility of Au containing oxide systems under study is determined by the properties of the supported Au particles.

High H$_2$ consumption peak can be attributed to the better reducibility, and resulting better redox properties as well as better thermal stability of the catalyst [10]. After depositing gold, it strongly interacts with the support, thus changing the reducibility of the support. The amount of hydrogen consumption in each of the studied catalysts decreased in the following order: Au/CeO$_2$-ZrO$_2$ > Au/CeO$_2$-ZrO$_2$-TiO$_2$ > CeO$_2$-ZrO$_2$ > Au/ZrO$_2$. The activity trend also follow the same order as discussed later on.

XPS measurements were used to identify the oxidation state of the Au species on different supports (Fig. 4). All gold containing samples showed two peaks, due to Au 4f5/2 and Au 4f7/2 signals. Metallic gold presence was registered at binding energy 83.64 eV and at 87.34 eV. These signals are result of the occurrence of Au 4f7/2 and Au 4f5/2 transitions. The peaks registered at binding energy of 85.27 eV and 88.97 eV respectively, which are result of the presence of Au$^{+1}$ species. No Au$^{+3}$ species were detected in the all gold containing samples. Deconvoluted spectrum of Au/ZrO$_2$ catalyst showed about 16 % of Au$^{+1}$ species and 84 % of metallic gold Au$^0$ on the catalyst surface. For the Au/CeO$_2$-ZrO$_2$ sample, the metallic Au$^0$ and oxidized gold percentages are almost the same, 47 % of Au$^{+1}$ and 53 % of metallic gold Au$^0$ on the surface. 31 % of oxidized to Au$^{+1}$ gold and 69 % of metallic gold are found on Au/CeO$_2$-ZrO$_2$-TiO$_2$ catalysts surface. Oxidized Au$^{+1}$ species percentage on the surface of studied gold catalysts were decreasing in the following order: Au/CeO$_2$-ZrO$_2$ (47 %) > Au/CeO$_2$-ZrO$_2$-TiO$_2$ (31 %) > Au/ZrO$_2$ (16 %). This order has similar trend with the amount of H$_2$ consumption by these three catalysts and also in their catalytic activities.
Catalyst activity performance

The catalytic activity and product selectivity data of partial oxidation of methanol (POM) over three gold containing catalysts Au/ZrO₂, Au/CeO₂-ZrO₂ and Au/CeO₂-TiO₂-ZrO₂ and on the CeO₂-ZrO₂ support are presented in supplementary Table (S1) and also depicted in Fig. 5. H₂ and CO were the main reaction products, H₂O and CO were by-products for all the catalysts tested in this study. Only trace amounts of formaldehyde were observed on CeO₂-ZrO₂ support in all used temperatures. Fig. 5 shows catalytic activity results for POM on the CeO₂-ZrO₂ support and on the Au/ZrO₂, Au/CeO₂-ZrO₂ and Au/CeO₂-TiO₂-ZrO₂ catalysts at different temperatures.

The catalytic activity for oxygen and methanol conversion and product selectivity of Au-ZrO₂ and on CeO₂-ZrO₂ support are very low compared to the same parameters of the Au/CeO₂-ZrO₂ and Au/CeO₂-TiO₂-ZrO₂ catalysts at the temperature range used in this study. O₂ conversion reaches over 99 % at a relatively low temperature (275 °C) for both of the Au/CeO₂-ZrO₂ and Au/ CeO₂-TiO₂-ZrO₂ catalysts, also showed high activity towards the methanol conversion. The activity of the tested Au catalysts increased with the increase of temperature and reaches values around 99 % at 450 °C on both catalysts. Nearly 50 % of methanol conversion and 31.6 % of H₂ selectivity were registered at temperature 275 °C for Au/CeO₂-ZrO₂ catalyst. The selectivity of H₂ increased with the increase of the temperature and reached maximal value of 75.8 % at 375 °C. Increasing of the CO selectivity with increase of the temperature was also observed and it reached maximum of 62.2 % at temperature 450 °C. The Au/ CeO₂-TiO₂-ZrO₂ catalyst showed lowest H₂ selectivity of 6.0% at temperature of 275 °C. It also was increased with the rise of temperature and reached value of 71.0 % of at 425 °C. Relatively lower H₂ selectivity was achieved at higher temperature compared to Au/CeO₂-ZrO₂ catalyst. Further increasing of the temperature leads to decrease of the selectivity to H₂ and increase CO selectivity. CO selectivity of this catalyst is very low at temperatures below of 350 °C. Above this temperature the CO selectivity jumps to a higher value of 13 %. The selectivity increases with the increase of temperature up to 450 °C with an end value of 57 %. There is no decrease on CO selectivity after 375 °C as it was seen for H₂ selectivity trend over Au/CeO₂-ZrO₂ catalyst, and above 425 °C for Au/CeO₂-TiO₂-ZrO₂ catalyst. It is the indication that the reverse WGSR takes place above these temperatures over these particular catalysts.

Discussion

The POM process proceeds simultaneously with different parallel reactions at different temperature ranges. At low temperatures there may be combination of the complete combustion (4) in the presence of excess oxygen followed by the methanol steam reforming reaction (5) to produce hydrogen:

\[
\text{CH}_3\text{OH} + 1.5\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad \text{Complete combustion} \quad (4)
\]

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2 \quad \text{Steam reforming} \quad (5)
\]

As temperature is increased the methanol decomposition (6) is increased and WGSR (7) starts to proceeds. The result is that we observe increase in hydrogen selectivity in our system.

\[
\text{CH}_3\text{OH} \rightarrow \text{CO} + \text{H}_2 \quad \text{Methanol decomposition} \quad (6)
\]

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad \text{Water gas shift reaction} \quad (7)
\]
At higher temperatures both methanol, oxygen are diminished from the system, therefore reverse water gas shift reaction starts to proceed. This explains the decrease in hydrogen selectivity at high temperatures (>400 °C). Moreover at low temperatures of (<325 °C) the low selectivity of hydrogen suggests that surface oxidation of hydrogen to water proceeds more selectively over these catalysts than the CO oxidation reaction according to CO\textsubscript{2} concentration data. Some activity and selectivity data found in the published papers regarding Au based catalyst for POM reaction have been tabulated in Table 3 in order to compare with the results of our best performed catalyst. According to the literature Au/CeO\textsubscript{2} [14] and Au/TiO\textsubscript{2} [15] catalysts didn’t show higher selectivity towards hydrogen, compared to our best performed catalyst, Au/CeO\textsubscript{2}-ZrO\textsubscript{2}, where we have attained 75.5 % of hydrogen selectivity at 375 °C.

For Au/TiO\textsubscript{2} catalyst, zero CO formation and 35 % of H\textsubscript{2} selectivity at 310 °C was attained when oxygen to methanol ratio was controlled at 0.3, but disadvantage of this catalyst is that it was deactivated very soon [15]. For other Au/CeO\textsubscript{2} catalyst CO selectivity values were not reported and also it is observed relatively lower H\textsubscript{2} selectivity at high temperature [14]. At low temperature (275 °C), Au/CeO\textsubscript{2}-ZrO\textsubscript{2} catalyst gave 7.5 % of CO selectivity with 31.60 % of H\textsubscript{2} selectivity, and at high temperature it exhibits better hydrogen selectivity and methanol conversion. In [16] it is reported that the best catalyst have 84 % selectivity for H\textsubscript{2} and about 20 % selectivity for CO with 98 % methanol conversion. However, these authors used another precious metal Ru in addition to Au.

**Figure 5:** Activity and selectivity plot for Methanol Partial Oxidation over CeO\textsubscript{2}-ZrO\textsubscript{2}, Au/ ZrO\textsubscript{2}, Au/CeO\textsubscript{2}-ZrO\textsubscript{2}-TiO\textsubscript{2} and Au/CeO\textsubscript{2}-ZrO\textsubscript{2} catalysts; temperature ranging from 275-450 °C, O\textsubscript{2}/CH\textsubscript{3}OH molar feed ratio 0.5 and GHSV = 30000 h\textsuperscript{-1}. 

At higher temperatures both methanol, oxygen are diminished from the system, therefore reverse water gas shift reaction starts to proceed. This explains the decrease in hydrogen selectivity at high temperatures (>400 °C). Moreover at low temperatures of (<325 °C) the low selectivity of hydrogen suggests that surface oxidation of hydrogen to water proceeds more selectively over these catalysts than the CO oxidation reaction according to CO\textsubscript{2} concentration data. Some activity and selectivity data found in the published papers regarding Au based catalyst for POM reaction have been tabulated in Table 3 in order to compare with the results of our best performed catalyst. According to the literature Au/CeO\textsubscript{2} [14] and Au/TiO\textsubscript{2} [15] catalysts didn’t show higher selectivity towards hydrogen, compared to our best performed catalyst, Au/CeO\textsubscript{2}-ZrO\textsubscript{2}, where we have attained 75.5 % of hydrogen selectivity at 375 °C. For Au/TiO\textsubscript{2} catalyst, zero CO formation and 35 % of H\textsubscript{2} selectivity at 310 °C was attained when oxygen to methanol ratio was controlled at 0.3, but disadvantage of this catalyst is that it was deactivated very soon [15]. For other Au/CeO\textsubscript{2} catalyst CO selectivity values were not reported and also it is observed relatively lower H\textsubscript{2} selectivity at high temperature [14]. At low temperature (275 °C), Au/CeO\textsubscript{2}-ZrO\textsubscript{2} catalyst gave 7.5 % of CO selectivity with 31.60 % of H\textsubscript{2} selectivity, and at high temperature it exhibits better hydrogen selectivity and methanol conversion. In [16] it is reported that the best catalyst have 84 % selectivity for H\textsubscript{2} and about 20 % selectivity for CO with 98 % methanol conversion. However, these authors used another precious metal Ru in addition to Au.
The present study shows that Au/CeO$_2$-ZrO$_2$ catalyst has highest catalytic activity for production H$_2$ among the tested four catalysts. The catalytic performance of these catalysts are arranged in the following decreasing order Au/CeO$_2$-ZrO$_2$ > Au/CeO$_2$-ZrO$_2$-TiO$_2$ > CeO$_2$-ZrO$_2$ > Au/ZrO$_2$. From TPR result we can see that after deposition of gold on the oxide supports, the catalysts have significantly lower the reduction temperature compared to the corresponding pure supports. Therefore, the gold is playing key role for changing the redox property of the Au containing catalysts. BET, XRD, TPR and XPS results indicate that the higher is the surface area, of gold dispersed on the surface, the higher are redox property of support and the higher is the amount of the Au$^{+1}$ species of gold. It is the main factor influencing catalytic performance of gold supported catalysts. Among the tested catalysts, Au/ZrO$_2$ has the lowest activity in POM because of the largest part of the surface gold atoms are in Au$^0$ state. This is result of Au interaction with ZrO$_2$ support. On the other hand, in Au/CeO$_2$-ZrO$_2$ metallic Au$^0$ and Au$^{+1}$ species are detected and surface presence of these two states of gold are in equal amounts. Therefore, it has the content of Au$^{+1}$ species relatively higher than in the other samples and for this reason it shows the best catalytic activity and hydrogen selectivity for POM reaction. Fig. 6 depicts a relationship that describes the influence of Au$^{+1}$ content on the catalyst surface on hydrogen selectivity at 400 $^\circ$C. As it is noticed, with the increase of the Au$^{+1}$ content on the catalyst surface, the selectivity of H$_2$ increases (Fig. 6). Obviously, the amount of oxidized gold species in the catalyst is playing important role in the POM process. Therefore all described above reactions i.e. methanol combustion, partial oxidation, steam reforming, reverse water gas shift and hydrogen combustion are taking place simultaneously. Decreasing the yield of hydrogen at higher temperature might be result of the proceeding of the reverse WGSR. Further research need to be conducted for studying in details the catalyst calcinations regime pre-treatment procedure, as well as the catalyst promotion by other elements.

### Table 2. Comparison of different gold based catalysts for POM reaction.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T (°C)</th>
<th>O$_2$:CH$_3$OH Mole ratio</th>
<th>CH$_3$OH conversion %</th>
<th>H$_2$ Selectivity %</th>
<th>CO Selectivity %</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au-Ru/Fe$_2$O$_3$</td>
<td>250</td>
<td>0.3</td>
<td>98.0</td>
<td>84</td>
<td>20</td>
<td>[16]</td>
</tr>
<tr>
<td>Au/TiO$_2$</td>
<td>250</td>
<td>0.3</td>
<td>80.0</td>
<td>35</td>
<td>15</td>
<td>[15]</td>
</tr>
<tr>
<td>Au/CeO$_2$</td>
<td>250</td>
<td>0.3</td>
<td>75.0</td>
<td>12</td>
<td>N/A</td>
<td>[14]</td>
</tr>
<tr>
<td>Au/ZrO$_2$</td>
<td>450</td>
<td>0.5</td>
<td>66.0</td>
<td>16.0</td>
<td>68.24</td>
<td>This work</td>
</tr>
<tr>
<td>Au/CeO$_2$-ZrO$_2$</td>
<td>375</td>
<td>0.5</td>
<td>91.6</td>
<td>75.5</td>
<td>22.30</td>
<td>This work</td>
</tr>
<tr>
<td>Au/CeO$_2$-ZrO$_2$-TiO$_2$</td>
<td>425</td>
<td>0.5</td>
<td>99.2</td>
<td>70.6</td>
<td>44.96</td>
<td>This work</td>
</tr>
</tbody>
</table>

The relationship between Au$^{+1}$ content (XPS) over different supports and hydrogen selectivity for partial oxidation of methanol at 375 °C, O$_2$:CH$_3$OH molar feed ratio 0.5 and GHSV = 30000 h$^{-1}$.
Conclusions

Au/CeO$_2$-ZrO$_2$ catalyst showed the best catalytic activity and H$_2$ selectivity for methanol partial oxidation among the investigated catalysts. The catalytic activity decreased in the following sequence Au/CeO$_2$-ZrO$_2$ > Au/CeO$_2$-ZrO$_2$-TiO$_2$ > CeO$_2$-ZrO$_2$ > Au/ZrO$_2$.

The same trend was observed in the catalysts reducibility and in percentage of Au$^{+1}$ content in the catalysts. At optimal temperature of 375 $^o$C we have observed 91.6% of methanol conversion, 75.5% of H$_2$ selectivity and 22.3% of CO selectivity for Au/CeO$_2$-ZrO$_2$ catalyst. Deposition of gold on CeO$_2$-ZrO$_2$ mixed oxide support strongly depresses its partial reduction and oxygen mobility.

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References

Gold Nanoparticles supported on CeO$_2$-ZrO$_2$ gives 75.5% H$_2$ selectivity at 375 $^\circ$C for partial oxidation of methanol reaction.