

Peculiarities of supported gold catalysts. The role of nano-environment in the activity control of supported gold catalysts.

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Introduction

Last fifteen years supported gold catalysts have obtained great general interest^{1,2}. Most of the authors consider that the key issue for high activity of supported gold catalyst is the stabilization of gold nano-clusters in the range of 2-4 nm. In this study we shall demonstrate that although the stabilization of gold in the above size range is very crucial, the nano-environment of gold controls the activity in CO oxidation. Consequently, the most crucial issue is finding the modes and ways to anchor various chlorine free entities into the support. These nano-entities serve as anchoring sites for the gold. In this lecture results using methods of conventional and high-throughput (HT) experimentation, spectroscopic investigations and high-resolution TEM measurements will be given and discussed.

Materials and Methods

Various methods were used to prepare the parent and the modified supports. HAuCl₄ was used as gold precursor applying common and modified deposition-precipitation method and decomposition by urea. *In situ* prepared amine complex was applied to introduce gold onto SiO₂. Continuous-flow isotherm and temperature programmed (TP) reactors were applied. Details on conventional and HT experimental methods used in CO oxidation can be found elsewhere^{3,4}. In TPO experiments: amount of catalyst. 25 – 75 mg, P_{CO} = 5 torr, P_{O₂} = 5 torr, heating rate 5 °C /min. In FTIR measurements CO was also used as a probe molecule to characterize supported gold both in the absence and presence of oxygen. High-resolution TEM was also applied to characterize the catalysts focusing on the gold nano-environment.

Results and Discussion

The influence of the pretreatment of Au/MgO catalyst at 350 °C in different atmosphere is shown in Figure 1. The treatment in H₂ and Ar resulted in the characteristic U pattern. Au/Al₂O₃ catalysts modified by MgO and Au/MgAl₂O₄ catalyst had similar U-shape. Contrary to that after pretreatment in O₂ significant activity decrease below 50 °C was observed. This decrease was completely removed after treatment in H₂ at 350 °C. The most striking observation is the strong activity increase after subsequent treatment in argon at 500 °C. The treatment in O₂ at 500 °C resulted in additional activity decrease below 50 °C and the loss of activity could not be restored after treatment in H₂ at 350 °C (see Figure 1). The modification of Au/MgO with V resulted in a slight activity decrease after treatment in H₂ at 350 °C, however the U pattern has been maintained as shown in Figure 2. The treatment in O₂ decreased the activity below 10 °C, but significantly increased it above this temperature. The higher the temperature of treatment in O₂ the higher the value of conversion in the U part. Analogous results were obtained upon modification by Ce, Sm and Pb.

The modification of Al₂O₃ catalysts with FeO_x, MnO_x, CoO_x, PbO_x and Sm₂O₃ resulted in also significant activity increase. Similar pattern was observed upon using the corresponding spinels of Fe, Mn, and Co. In the latter catalysts no correlation was obtained between the activity and the particle size measured by TEM. As a conclusion the activity of MgO and Al₂O₃ supported modified gold catalysts was strongly altered by reductive or oxidative pretreatments. Results of *in situ* FTIR measurements support the above findings.

The high activity of Au/MgO catalyst below room temperature has been attributed to the formation of Au⁻⁸-Au⁰ ensemble sites. These sites loss their activity upon increasing the reaction temperature and they are very sensitive to O₂, it is the reason the pre-treatment in O₂ decreases the activity below 25 °C. Upon introduction of redox metals (M) new types of ensemble sites (Mⁿ-Au⁰) are created. These sites show high activity above 50 °C.

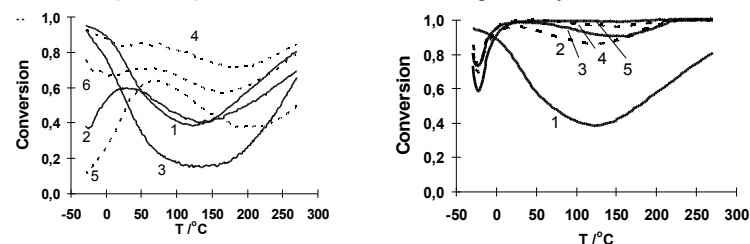


Figure 1. TPO oxidation of CO over Au/MgO catalyst after different treatments. 1 – H₂, 2 – O₂, 3 – Ar (all at 350 °C), 4 – H₂ 350 °C and Ar –500 °C, 5 – O₂ – 500 °C, 6 – after 5: H₂ – 350 °C.

Figure 2. TPO oxidation of CO over Au/VOx-MgO catalyst after different treatment procedures. 1- H₂ – 2- 5 in O₂ after 350, 380, 400 °C and 450 °C, respectively

Upon modification of Al/Al₂O₃ catalysts by Pb and Sn alloy formation was evidenced. High resolution TEM results clearly show that nano-sized gold clusters are located in the vicinity of nano-layers of oxides introduced as modifiers.

Significance

Based on these findings new types of modified Au/MgO⁴ and Au/Al₂O₃⁵ catalysts were designed for PROX application using combinatorial and HT approaches. The compositions of the best hits were not known earlier. The results showed that not only the composition, but the condition of the pretreatment were crucial to get highly active supported gold catalysts.

References

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