

RKCL5242

**THE ROLE OF THE NANO-ENVIRONMENT OF SUPPORTED GOLD
CATALYSTS IN THE ACTIVITY CONTROL. MODIFICATION OF
Au/Al₂O₃ CATALYSTS BY REDOX-TYPE METAL OXIDES**

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Received November 14, 2007, accepted November 29, 2007

Abstract

Au/Al₂O₃ catalysts were modified by different redox metal oxides, such as FeO_x, MnO_x and CoO_x, resulting in a pronounced activity increase in CO oxidation.

Keywords: Au/Al₂O₃, catalyst modification, redox metal oxides, CO oxidation

INTRODUCTION

In the last 10-15 years the interest for supported gold catalysts has greatly increased due to their high activity in low-temperature CO oxidation [1,2]. It has been demonstrated by different research groups that the support has a great influence on the activity of supported nano-sized gold [2]. It has been shown that gold stabilized over alumina [3] and silica [4] are much less active than gold supported on redox metal-oxides [2,5].

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We demonstrated recently that Au/MgO catalysts could effectively be modified both by iron and manganese [6]. The modification increased the activity in the temperature range of 30 – 100°C. As a continuation of this approach, Au/Al₂O₃ catalysts with different Au contents were modified by iron, manganese and cobalt with the aim to increase the activity in the temperature range of -30 to 270°C.

The main goal of this study is to demonstrate that "metal ion – metal nano-cluster" ensemble sites [7] formed after modification of Au/Al₂O₃ catalyst by redox metal oxides are involved in the activity increase. In other words, we would like to demonstrate that the Au-support interaction has a crucial role in the activity control.

EXPERIMENTAL

Alumina support prepared as described earlier [8] (unit surface area = 360 m²/g) was used for the preparation of parent and modified Au/Al₂O₃ catalysts. Solutions of nitrates of the precursor compounds (5.1 mL/g Al₂O₃) were used for the modification of alumina. After calcination at 450°C and subsequent cooling the support was poured into the impregnating solution and kept at 50°C for one hour under stirring. After decantation the solid was dried at 50°C for 18 hours followed by calcination using the following temperature ramp: heating to 130°C with a heating rate of 8°C/min and keeping thus for 2 hours, followed by further heating to 450°C with a heating rate of 3.5°C/min and kept at this temperature for 2 hours.

Both the parent and modified Au/Al₂O₃ catalysts were prepared by the impregnation method using H₂AuCl₄•3H₂O (Fluka) at pH = 8.5 [9]. The gold-containing samples were dried at 64°C and reduced prior to the catalytic experiments in hydrogen at 350°C and cooled in helium.

Temperature Programmed Oxidation technique was used to investigate the activity of the catalysts in the temperature range of -30 to 270°C. This method is often applied when the activity of different catalysts has to be compared in a broad temperature range. Further details can be found elsewhere [10]. The conditions of CO oxidation were as follows: heating rate: 5°C/min, carrier gas: helium, amount of catalyst: 75 mg, total flow rate: 70 cm³/min, P_{CO} = 16 torr, P_{O₂} = 44 torr. MS analysis was used to follow the CO conversion. Two measured values were used for the comparison of modified catalysts: (i) T₅₀ (temperature required for 50% conversion, and (ii) conversion values at -30°C. Some of the catalysts were so active that the T₅₀ values could not be evaluated.

X-ray powder diffraction (XRPD) patterns were obtained in a Philips model PW 3710 equipment as described earlier [11]. XRD results indicated that the particle size of gold both in the parent Au/Al₂O₃ and the modified Au/Al₂O₃ catalysts was below 4.0 nm.

RESULTS AND DISCUSSION

The comparison of the TPO pattern of selected Au/Al₂O₃ catalysts modified by different redox metal oxides is shown in Fig. 1. This figure shows clearly the positive influence of modification. For comparison, the result obtained over Au/Al₂O₃ catalyst modified by MgO is also presented [12].

Table 1

Temperature programmed oxidation of CO over Au/Al₂O₃ catalysts modified by MnO_x, CoO_x and FeO_x

N°	Catalysts	Activity	
		T ₅₀ (°C)*	K ₋₃₀ (%)**
1	1.6 Au/Al ₂ O ₃	120	37
2	2.4 Au/Al ₂ O ₃	100	38
3	1.6 Au/ 2.9 Mn-Al ₂ O ₃	26	35
4	2.6 Au/ 3.1 Mn-Al ₂ O ₃	-	85
5	1.7 Au/ 4.2 Mn-Al ₂ O ₃	41	34
6	2.6 Au/ 4.2 Mn-Al ₂ O ₃	-	82
7	2.4 Au/ 5.2 Mn-Al ₂ O ₃	16	36
8	1.6 Au/ 4.0 Co-Al ₂ O ₃	-22	61
9	2.1 Au/ 4.0 Co-Al ₂ O ₃	-	65
10	1.4 Au/ 6.7 Co-Al ₂ O ₃	-2	50
11	2.0 Au/ 6.7 Co-Al ₂ O ₃	-6	50
12	1.7 Au/ 2.1 Fe-Al ₂ O ₃	-14	35
13	2.7 Au/ 2.1 Fe-Al ₂ O ₃	-	87
14	1.6 Au/ 3.5 Fe-Al ₂ O ₃	-8	36
15	2.6 Au/ 3.5 Fe-Al ₂ O ₃	-	84
16	1.6 Au/ 6.0 Fe-Al ₂ O ₃	-5	26
17	2.7 Au/ 6.1 Fe-Al ₂ O ₃	-	68

* temperature required for 50% conversion; ** conversion at -30°C.

„-“, – the minimum conversion value is higher than 50%.

Further activity data over modified catalysts are given in Table 1. The gold content of the catalysts was around 1.4-1.6 and 2.0-2.7 wt.%, while the redox metal oxide content was in the range of 2.1-6.7 wt.%. As is seen from the results presented in Table 1, the modification of Au/Al₂O₃ with redox metal oxides resulted in a significant activity increase in the whole temperature interval. In most of the modified samples, T₅₀ could not be determined, as the initial activity at -30°C was higher than 50%. The effectiveness of the modifiers increased in the following order: Co<Mn<Fe.

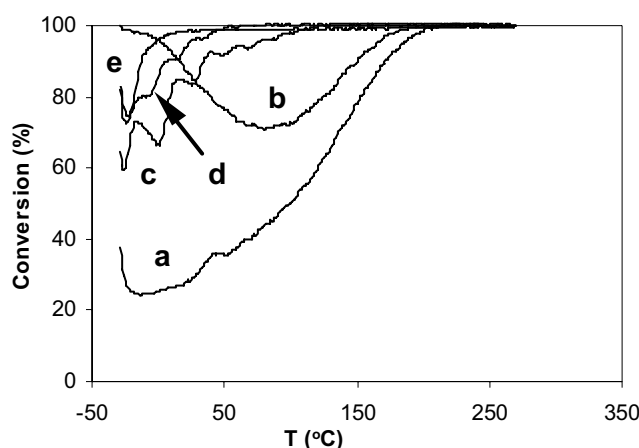


Fig. 1. Temperature Programmed Oxidation of CO in the presence of Au/Al₂O₃ catalysts modified by various redox metals and MgO. **a** – 2.4%Au/Al₂O₃; **b** – 2.6%Au/8.4%MgO-Al₂O₃; **c** – 2.1%Au/4.0%Co-Al₂O₃; **d** – 2.6%Au/4.2%Mn-Al₂O₃; **e** – 2.6%Au/3.5%Fe-Al₂O₃

Analysis of the results given in Fig. 1 shows that there is only a small difference between the modifiers, although in this series FeO_x showed the most pronounced effect. As shown by Fig. 1, the activity of parent Au/Al₂O₃ in the sub-ambient temperature range is low and the TPO pattern shows a monotonic increase type activity - temperature dependence. In selected modified samples containing Co and Mn periodical oscillations were observed. It is suggested that the oscillations are due to the periodical change of the valence state of the modifier during the oxidation reaction. This is possible as the surface coverage of CO and oxygen is not constant, it is the function of temperature. The low redox potential of these metals makes the fluctuation of the valence state during the TPO run possible. Further studies in this respect are in progress.

In case of Mn and Fe modified catalysts, at low Au content the initial activity at -30°C is almost independent of the presence or absence of the modifier added (compare catalysts No. 1, 3, 5, 8, 10, 12, 14, 16 in Table 1). Co

modified catalysts has slightly higher initial activity than the parent Au/Al₂O₃ catalyst (compare samples No. 1 and 8, 10). However, at high gold content the influence of the modifier is well seen in all cases.

There is a general trend in case of all modifiers, *i.e.*, upon increasing the concentration of the modifier the activity passes through a maximum. It means that in all cases there is an optimum modifier concentration. It is suggested that at high modifier concentration the chance of forming large Au particles increases due to the spontaneous reduction of the anchored gold precursor by the modifier introduced. Preliminary TEM results confirmed this suggestion, *i.e.*; the particle size of modified catalysts is slightly larger.

The addition of MgO to Al₂O₃ alters the TPO pattern in a different way, *i.e.*, the characteristic U-shaped TPO profile appears [12]. The TPO profile of Au/MgO-Al₂O₃ catalyst is similar to that of the Au/MgO catalyst in the whole temperature range [6,12,13]. This finding indicates that the effect of the modifier strongly depends on its intrinsic properties, consequently, the intrinsic properties of redox metal oxides and MgO are completely different.

When cooling the catalyst in TPO experiments, the activity decreases for both parent and Fe and Mn modified catalysts in the whole temperature region, however the activity of modified catalysts is still higher than that of the parent Au/Al₂O₃. Under similar conditions Co shows a slight activity increase at high temperature, while a decrease at low temperature. These facts might indicate that the valence state of the modifier has also a definite influence on the overall activity. However, subsequent reduction in hydrogen at 350°C completely restores the initial activity.

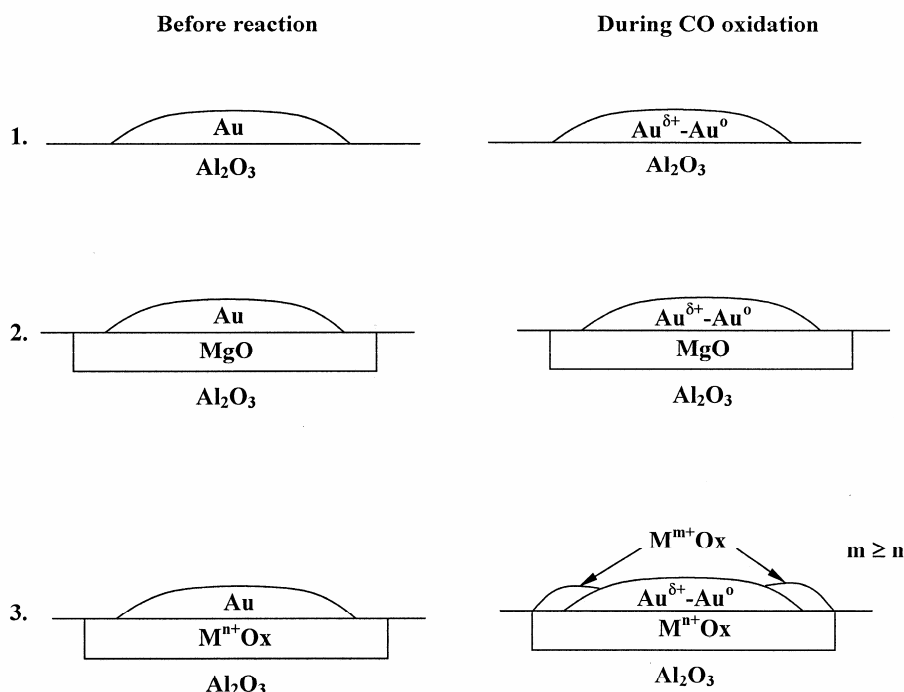
SUMMARY

Based on results on Sn-Pt/SiO₂ [14] and Au/MgO [6,12] catalysts, we have proposed a new mechanism for CO activation with the involvement of "metal ion – metal nano-cluster" ensemble sites [7]. Over Sn-Pt/SiO₂ catalysts the formation of surface Sn⁴⁺, while on Au/MgO catalysts ionic forms of gold (Au^{δ+}) were evidenced by different *in situ* spectroscopic methods. According to this concept, a metal ion stabilized in the neighbourhood of a supported metal nano-cluster interacts with the lone electron pair of the oxygen atom of the chemisorbed CO molecule. The net result of this interaction is a perturbation of the CO molecule leading to its high reactivity even at low temperatures. This concept has been recently extended to the Fe-MCM41 type catalyst, which showed high activity in low temperature CO oxidation after its reduction in hydrogen above 500°C [15].

We suggest that the formation of "metal ion – metal nano-cluster" ensemble sites can also take place in different supported gold catalysts, especially in those

containing active supports, such as TiO_2 , MnO_2 , Fe_2O_3 , *etc.* A similar kind of interaction is expected when Al_2O_3 is modified by redox-type metal oxides.

The introduction of 6 wt.% MgO into the support resulted in almost 100% conversion at -30°C . The increase of the temperature resulted in fast activity decrease, although the lowest activity measured around 80°C was still much higher than that of the parent $\text{Au}/\text{Al}_2\text{O}_3$ catalyst. Further increase of the temperature resulted in an activity increase resulting in a well-expressed U-type temperature dependence.



Scheme 1

Completely different activity pattern was obtained upon introduction of redox metals, such as Fe, Mn and Co. We suggest that the addition of redox metal oxides creates a new nano-environment for gold as shown in Scheme 1. We admit that not all gold nanoclusters have the new nanoenvironment, however, preliminary high resolution TEM-EDAX results clearly demonstrate the intimate contact between gold and the metal oxides used as modifier [16].

We propose that in the absence of modifier the activation of CO and its oxidation takes place at the Au nano-cluster. However, this activation does not

result in high activity when gold is deposited onto alumina. When redox metals are introduced the activation of CO can also take place at the interface between gold and the redox metal oxide. This new interaction is responsible for the increased activity. This behavior is shown in Scheme 1. This scheme shows the difference between the parent and modified catalysts. The activity of modified catalysts is strongly affected by the type of modifiers. In this respect, redox metal oxides behave in a similar way, while MgO provides a completely new character in the TPO run. In both cases the nano-environment of gold is altered. With respect to the form of this nano-environment either islands of the oxides applied can be suggested. These oxides are finally dispersed over alumina, as their detection by XRD was unsuccessful. Alternatively, it can also be suggested that during the calcination step, prior to the introduction of gold, nano-sized spinel phases are formed. In our next communication the use of spinels of Mg, Fe, Co, and Mn as potential supports for gold will be demonstrated [17].

Acknowledgement. The authors greatly acknowledge István Sajó for the accomplishment of XRD measurements on selected modified catalyst samples.

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