

Supported gold catalysts for the decomposition of Volatile Organic Compounds: Total oxidation of propene at low concentration

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Introduction

Emission of volatile organic compounds (VOC) arising from domestic or industrial activities leads to air pollution. Gas streams requiring treatment often contain only low concentrations of VOC (100-2000 ppm), and catalytic combustion is a promising technology for the destruction of VOCs. Supported noble metals (Pt, Pd, Rh) and transition metal oxides such as cobalt, chromium, or manganese oxides are the two categories of catalysts active for VOCs decomposition. Gold-based catalysts, which have been more recently investigated, are also promising for this type of issue [1-3]. The goal of the study was to explore the properties of gold catalysts supported on various oxides in the reaction of oxidation of propene in low concentration, so as to mimic the conditions of catalytic decomposition of a hydrocarbon-type VOC. Parameters directly related to the nature of the catalysts were investigated: nature of the support, gold loading, activation conditions and oxidation state.

Materials and Methods

Gold catalysts (1 wt% Au) were prepared by deposition-precipitation with urea [4], using TiO₂ (45 m²/g), Al₂O₃ (110 m²/g) and CeO₂ (250 m²/g) as supports. Gold on ceria was also prepared with two other loadings, 0.02 and 4 wt %. Before reaction, the samples were activated *in situ* either under hydrogen at 300 °C or under O₂/He at 500 °C. XPS analyses and the reaction of CO oxidation (CO ox, 1% CO / 9% O₂ /He) at room temperature were used to characterise the oxidation state of gold. Indeed, it has been shown that activity in CO oxidation at RT requires both the presence of metallic gold and of a reducible support [5]. The reaction of propene oxidation (C₃H₆ ox, 1200 ppm C₃H₆ / 9% O₂ /He) was performed in isothermal conditions by stepwise increase of the temperature up to 500 °C. Under these reaction conditions, the selectivity to CO₂ was 100%.

Results and Discussion

Titania and alumina alone do not show any conversion in C₃H₆ ox up to 500°C, but when gold was added (1 wt %), they become active with a higher activity for titania than for alumina. Ceria is the only support showing activity, and gold on ceria (1 wt %) leads to the most active catalyst (Table 1). For the Au/CeO₂ system, activation under H₂ at 300°C leads to more active catalysts, than calcination. This is especially visible for the low gold loadings (≤1 wt %) (Table 1). XPS and CO ox at RT show that gold on CeO₂ is fully reduced to Au⁰ after reduction whatever the gold loading. They also showed that after calcination, most of the gold remained under the initial Au^{III} state for the ≤1 wt% samples) whereas most of it was reduced for the 4 wt% Au/CeO₂. Metallic gold is therefore more active than Au^{III} for C₃H₆ ox.

Change in the gold oxidation state was detected on calcined Au/CeO₂ (1 wt%) during C₃H₆ ox performed at increasing temperature, and interrupted by sample cooling to RT and reaction of CO ox at RT. Figure 1 shows that when the catalyst starts to be active in C₃H₆ ox, it also becomes active in CO ox, indicating that gold, initially Au^{III}, starts reducing. At

200°C, when 100% conversion of propene is reached, CO activity at RT is also maximum. Above 200°C, and especially between 300 and 500°C, activity in CO ox drops. Such a decrease in activity could be due either to a reoxidation of metallic gold or to an increase of the gold particles size under the reaction mixture. This will be clarified. These observations indicate that gold is readily reduced in the conditions of C₃H₆ ox and that metallic gold is the active species.

Table 1: Dependence of the T_{50%} (temperature at which the propene conversion reaches 50%) with the support, the gold loading and the activation treatment

1 wt % Au catalyst	Activation	T _{50%} (°C)	Au/CeO ₂ Au loading (wt %)	Activation	T _{50%} (°C)
Au/Al ₂ O ₃	Calcination	420	0.02	Calcination	245
				Reduction	210
Au/TiO ₂	Calcination	320	1	Calcination	170
				Reduction	160
Au/CeO ₂ (CeO ₂)	Calcination	170 (340)	4	Calcination	140
				Reduction	140

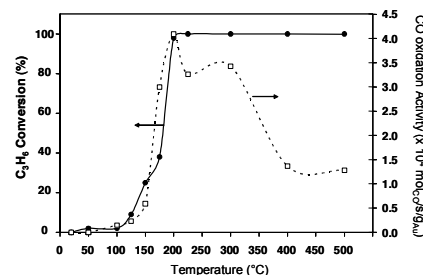


Figure 1. Conversion of propene versus temperature and activity in CO oxidation at RT performed after each measurement of propene conversion over calcined Au/CeO₂ (1 wt%).

This study shows that ceria is a very appropriate support for total oxidation of propene over gold catalysts. XPS and CO oxidation reveal that the oxidation state of gold supported on ceria depends not only on the activation treatment but also on the gold loading. Ceria seems to be able to stabilize gold as Au^{III} up to a limited loading. Propene can be totally converted in CO₂ at temperature as low as 200°C on Au/CeO₂. Activation under H₂ is beneficial to the activity, indicating that Au⁰ is required for the reaction. This is supported by the observation that Au^{III} initially present in calcined Au/CeO₂ is reduced during the reaction.

References

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