Supported gold catalysts effective for formaldehyde oxidation at room temperature

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Introduction

Given that formaldehyde is a major indoor air pollutant, significant efforts have been directed at indoor HCHO removal to meet environmental regulations and human health needs [1-3]. Catalytic oxidation is recognized as the most promising HCHO removal technology. Moreover, in our previous study, 1% Au/CeO₂ catalyst was found to provide 100% HCHO conversion at room temperature (RT) [4]. However, γ -Al₂O₃ is considered to be a poor support for low temperature HCHO oxidation catalysts due to its irreducibility. In recently, we firstly reported that γ -Al₂O₃ supported Au was also a very active catalyst for HCHO oxidation at RT even in the presence of water [5].

Herein, we present results of a comparative study on the catalytic properties of reducible oxide (CeO₂, FeO_x) and irreducible oxide (γ -Al₂O₃) supported gold catalysts for the HCHO oxidation. By employing the technique of in situ DRIFTs, we investigated the reaction mechanism and identified the rate-limiting step of HCHO oxidation over supported Au catalysts.

Materials and Methods

 Au/CeO_2 and $Au/\gamma-Al_2O_3$ catalyst with nominal gold loading of 1 wt. % were prepared by the deposition-precipitation method, using urea as precipitant, according to the procedures described in the previously reported literatures [4].

lwt % Au/FeO_x catalyst was prepared by co-precipitation of an aqueous solution of HAuCl₄ and Fe(NO₃)₃ with an aqueous solution of Na(CO₃)₂. The resulting precipitate without Cl was dried 60 °C for 12 h and then calcined in air at 200 °C for 4h.

Results and Discussion



Figure 1 TEM images of A) 1 wt%Au/CeO2; B) 1 wt%Au/FeO2; C) 1 wt%Au/γ-Al2O3 catalysts

- ♦ The mean particle size of Au-NPs was determined to be in the range of 2-4 nm in the Au/CeO₂ catalyst.
- ♦ The Au species were highly dispersed and the average particle size was 3-4 nm in the Au/FeO_x catalyst.
- The gold nanoparticles are highly dispersed on the γ-Al₂O₃ surface and an average of particle size of 2 nm was determined from the TEM images.



Figure 2 Comparison of reaction rates of HCHO oxidation over $0.3wt\%Au/CeO_2$, $0.5wt\%Au/FeO_x$ and $0.5wt\%Au/\gamma-Al_2O_3$ catalysts in 80 ppm HCHO/21%O₂/H₂O (RH=50%)/N₂ at RT, GHSV=34,000 h⁻¹

Figure 3 Arrhenius plots of reaction rates for oxidation of HCHO over the 1wt% Au/FeO_x catalyst at different relative humidity.

- Irreducible oxide supported gold catalyst showed the highest reaction rate of HCHO oxidation at RT.
- > The highly dispersed Au played a key role in the oxidation of HCHO at RT.
- Table 1 Reaction rate and Apparent activation energies (Ea) for the oxidation

Relative Humidity	d _{Au} a (nm)	Reaction Rate (µmol·s ⁻¹ ·g(Au) ⁻¹) ^b	Ea(kJ·mol ⁻¹)
Dry gas	3.5	0.21	172.1
25%	3.5	7.55	56.95
50%	3.5	10.78	51.79
75%	3.5	9.70	55.84

- ★ The apparent activation energy (*Ea*) of the HCHO oxidation was very high in dry gas condition. However, the *Ea* was greatly decreased in humid gas.
- ★ The change of Ea should be associated with the change of the reaction pathway.
- ★ Introduction of humidity provides another pathway for complete oxidation of HCHO.

Significance

- Reducible/irreducible oxide supported Au catalysts could oxidized of HCHO into CO₂ and H₂O at room temperature in the wet air.
- Surface oxygen and hydroxyl species played key role in the catalytic oxidation of HCHO.
- The consumption of the formate intermediates is the rate limiting step for catalytic oxidation of HCHO over Au/M_xO_y catalysts, which is catalyzed by the highly dispersed Au.
- Presence of moisture provides another reaction pathway with lower activation energy for Au/M_xO_y catalysts.

References

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