Temperature-Dependent Activation Properties for Carbon Monoxide Oxidation by Polyoxometalate-Supported Gold Nanoparticulate Catalysts

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Abstract: Nanoparticulate gold supported on Keggin-type polyoxometalate, $Cs_4[\alpha\text{-}SiW_{12}O_{40}]\cdot nH_2O$, was prepared by the sol immobilization method. The size of the gold nanoparticles was approximately 2 nm, which was almost the same as the size of the gold colloid precursor. Deposition of gold nanoparticles smaller than 2 nm onto polyoxometalate was essential for a high catalytic activity for CO oxidation. The temperature for 50% CO conversion was −67°C. The catalyst showed extremely high stability at least for 1 month at 0°C with full conversion. The catalytic activity and the reaction mechanism drastically changed at higher than 40°C, showing the unique behavior called U-shaped curve.

Keywords: Gold nanoparticulate, Polyoxometalate, CO oxidation.

1. Introduction

Preparation of nanoparticulate gold catalysts (NPGCs) is an active field of research.[1] It is intriguing that small gold nanoparticles (NPs) with diameters of 5 nm or less have shown high catalytic activity for various reactions. Polyoxometalates (POMs) are molecular metal oxide salts that have attracted considerable attention and the preparation of POM-based materials has been studied in various fields. However, there have been few reports on utilization of POMs as support materials for the deposition of gold.[2-4] However, the reported procedures for the preparation of Au/POMs have several problems. Many POMs are easily decomposed in an alkaline condition. Therefore, it is difficult to deposit gold NPs of less than 2 nm in size (so-called clusters) on the POM by the DP method in an alkaline condition. Also, chloride ion contained in the gold precursor markedly enhances the agglomeration of gold on the support material during calcination. Thus, we used the sol immobilization (SI) method with thiolate-protected gold colloids to prepare POM-supported NPGCs under chloride-free and non-alkaline conditions.

2. Experimental

SI was performed according to the literature[5] with slight modification. A dark brown solution of thiolate-protected gold colloids dissolved in 15 mL of toluene was added dropwise into a solution of Cs-SiW dispersed in 10 mL of toluene. After stirring for 1 h at room temperature, the solvent was evaporated to dryness with a rotary evaporator at 40°C. The dried catalyst was calcined at 300°C for 2 h in air. Gold colloids of several sizes (2.0, 4.2 and 10.7 nm = x) were prepared and the size was determined by transmission electron microscopy images. The obtained samples were denoted as Au(x)/Cs-SiW. The gold loadings determined by atomic absorption spectroscopy were 0.66wt% for Au(2.0)/Cs-SiW, 0.93wt% for Au(4.2)/Cs-SiW and 0.67wt% for Au(10.7)/Cs-SiW.

The catalytic activity for CO oxidation was measured by using a fixed-bed flow reactor. The reactant gas, 1vol% CO in air (50 mL min^{-1}), was fed to the catalyst (0.15 g). Moisture concentration downstream of the reactor was monitored as a dew point by using a dew point meter (AIR LIQUIDE Japan DPO-6), and the concentrations calculated from the dew point were 30–150 ppm in all experiments. The outlet gases were analysed by on-line gas chromatography (Agilent 490 Micro GC) to obtain both the conversion of CO and the formation of CO_2.

3. Results and discussion

The results for CO oxidation over Au(x)/Cs-SiW (x = 2.0, 4.2 and 10.7) are shown in Figure 1. The activity of Au(2.0)/Cs-SiW for CO oxidation was very high, and the conversion of CO was 100% even at −20°C. The temperature for 50% CO conversion ($T_{1/2}$) was −67°C. Au(2.0)/Cs-SiW is a very active NPGC for CO oxidation compared to previously reported NPGCs such as Au/TiO_2, Au/Fe_2O_3 and Au/Co_3O_4. The activity of Au(4.2)/Cs-SiW was drastically decreased compared to that of Au(2.0)/Cs-SiW, and $T_{1/2}$ was 16°C. Au(10.7)/Cs-SiW showed very little activity for CO oxidation. The results clearly showed that deposition of smaller gold NPs is essential to obtain an active Au/Cs-SiW catalyst for CO oxidation reaction. Interestingly, the activities of Au/Cs-SiW catalysts decreased with increase in the reaction temperature to more than 40°C. When the reaction temperature was higher than 140°C, the conversion gradually increased. The apparent activation energy (E_a) of Au(2.0)/Cs-SiW also varied depending on the temperature. Within the temperature range from −60 to 40°C, E_a was 20.9 kJ mol^{-1}. In the temperature range from 40 to 140°C, E_a was −25.0 kJ mol^{-1}. At the reaction temperatures of more than 140°C, E_a was 9.3 kJ mol^{-1}. These results indicate that there is a U-shape for the temperature dependence of activity. Figure 2 shows the relationship between CO conversion and reaction time at several temperatures. At lower temperatures (−40°C and −30°C), the conversion of CO was not changed after reaction for 6 h. The Au(2.0)/Cs-SiW catalyst showed full conversion with reaction for at least 840 h (35 days) at 0°C. The turnover number (TON) was more than 200,000 based on gold for 35 days. On the other hand, the conversion of CO at 60 and 80°C decreased by 15–20% after reaction for 12 h. Since the conversion recovered and showed 100% at room temperature after reaction for 12 h, those behavior are not due to deactivation of Au(2.0)/Cs-SiW catalyst itself. From the relationships among CO conversion, dew point during the reaction and reaction time. The results showed that the decrease of CO conversion at 60 and 80°C corresponded well to the decrease of the dew point. These results indicate that a small amount of water (less than 150 ppm) contained in the reaction gas is involved in the CO oxidation reaction by the Au(2.0)/Cs-SiW catalyst.

4. Conclusions

In conclusion, a high level of activity for CO oxidation at temperatures below room temperature and a unique activation curve for the temperature dependence were shown by using an Au/Cs-SiW catalyst, in which gold NPs of less than 2 nm in size were deposited on Cs-SiW. The conversion of CO was 100% even at −20°C, and full conversion was maintained for more than 840 h at 0°C.

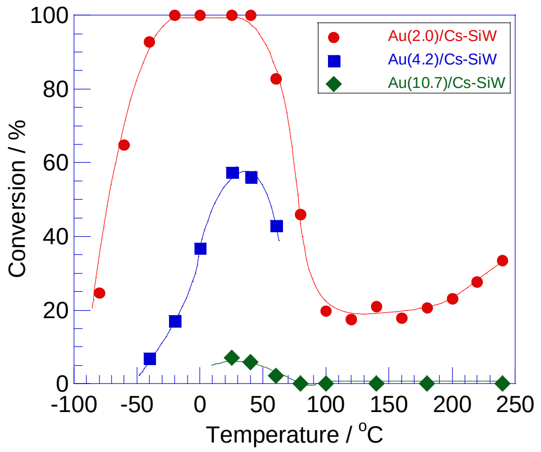

Figure 1. Effects of reaction temperature on CO oxidation over Au(2.0)/Cs-SiW, Au(4.2)/Cs-SiW and Au(10.7)/Cs-SiW catalysts.

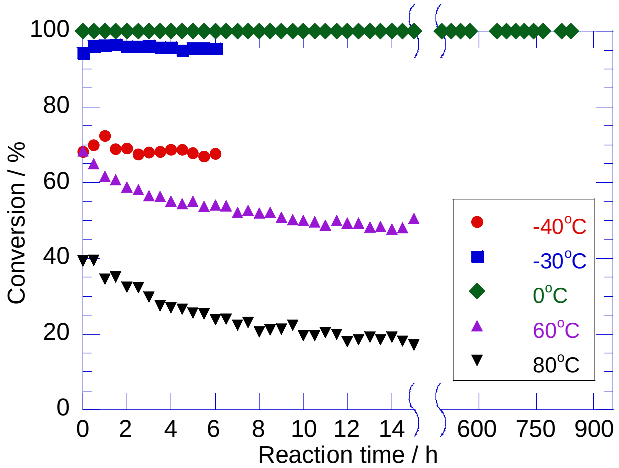

Figure 2. Catalytic stability of Au(2.0)/Cs-SiW for CO oxidation at −40, −30, 0, 60 and 80°C.

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