Polyoxometalate-Supported Gold Nanoparticulate Catalysts Prepared by sol immobilization method and their catalytic activity

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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.¹ 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. We used the sol immobilization (SI) method with thiolate-protected gold colloids to prepare POM-supported NPGCs under chloride-free and non-alkaline conditions.

SI was performed according to the literature² 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 (Cs₄SiW₁₂O₄₀) dispersed in 10 mL of toluene. 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 HAADF-STEM 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, 1 vol% CO in air (50 mL min⁻¹), was fed to the catalyst (0.15 g).

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 (T₁/₂) was −67°C. Au(2.0)/Cs-SiW is a very active NPGC for CO oxidation compared to previously reported NPGCs such as Au/TiO₂, Au/Fe₂O₃, and Au/Co₃O₄. The activity of Au(4.2)/Cs-SiW was drastically decreased compared to that of Au(2.0)/Cs-SiW, and T₁/₂ 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 (Ea) of Au(2.0)/Cs-SiW also varied depending on the temperature. Within the temperature range from −60 to 40°C, Ea was 20.9 kJ mol⁻¹. In the temperature range from 40 to 140°C, Ea was −25.0 kJ mol⁻¹. At the reaction temperatures of more than 140°C, Ea was 9.3 kJ mol⁻¹. These results indicate that there is a U-shape for the temperature dependence of activity. 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.

References


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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.