Gold nanoparticles stabilized by a flake-like Al₂O₃ support

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Abstract A flake-like alumina with rough surface and small mesopores has been prepared by a hydrothermal method. Remarkably, such alumina was able to stabilize Au nanoparticles, predominantly ∼2.2 nm in size, even up to an annealing temperature of 700°C. The catalytic activity was tested using the CO oxidation model reaction where a complete conversion of 1% CO in air at 30°C was obtained.

Keywords Thermostability · Alumina · Gold catalyst · CO oxidation

Introduction Supported gold catalyst with the gold nanoparticles predominantly below 5 nm in size was discovered to be active for many reactions [1–4]. These catalysts however commonly suffer from high temperature sintering, due to the low Tammann temperature (395°C) of gold, resulting in a significant loss of catalytic activity [5]. Thus, their application is limited where high reaction temperatures are required to prevent catalyst sintering, one feasible solution is to use mesoporous materials [6–9] and hollow cages [10, 11] to provide confined microenvironments for supporting the catalyst. Another is to prepare composite supports by intergrating the advantages of different materials, thus improving the thermal stability and activity of the gold catalyst [12–16]. Examples are CeO₂-doped mesoporous Al₂O₃ [12] and FeOₓ-modified hydroxyapatite [16].

Experimental

Preparation of Au/Al₂O₃ catalyst

Al(NO₃)₃·9H₂O was dissolved in deionized water. Urea was added to the solution as precipitating agent and stirred for 10 min. The molar ratio of Al(NO₃)₃: urea was 1:9, and the molar concentration of Al³⁺ was 0.02 M. The obtained solution was decanted into a stainless steel autoclave with a teflon liner and heated at 100°C for 24 h, followed by cooling to room temperature. A white precipitate was filtered and dried at 80°C for 12 h and then denoted as A1-hydro. Calcination of A1-hydro in air at 500°C for 2 h with a heating rate of 1°C min⁻¹, generated product, named as A1-500. For comparison, a conventional Al₂O₃ precursor was prepared by a common precipitation method using 0.02 M Al(NO₃)₃·9H₂O aqueous solution as precursor and 0.5 M (NH₄)₂CO₃ solution as precipitant under a pH of 8–9. After drying, this precipitant was named as A2-precip. Its calcined counterpart was denoted as A2-500.

Au/Al₂O₃ catalysts were prepared by a deposition–precipitation (DP) method using a HAuCl₄ solution at pH 8–9 (adjusted by 0.5 M (NH₄)₂CO₃ solution) in 80°C for 4 h. The samples were washed three times with deionized water, then once with alcohol followed by centrifugal separation and drying in a vacuum. Finally, the samples...
were annealed under a flow of air at 250°C or 700°C for 2 h to obtain Au/Al2O3 catalysts.

Catalytic test

The catalytic activity of Au/Al2O3 in CO oxidation was tested in a fixed bed quartz reactor using 50 mg of catalyst. The total flow rate of the reaction gas was 67 mL min⁻¹ with a composition of 1 vol.% CO, 20 vol.% O2, and 79 vol.% N2, corresponding to a space velocity of 80,000 mL h⁻¹ gcat⁻¹. The products were analyzed using a GC-7890 gas chromatograph equipped with a thermal conductivity detector.

Catalytic characterization

Thermogravimetric and differential scanning calorimetry analyses (TG-DSC) were conducted on a thermogravimetric analyzer STA 449 F3 Jupiter (NETZSCH) under an air atmosphere with a heating rate of 10°C min⁻¹. Transmission electron microscope (TEM) images were obtained with a Tecnai G220 S-Twin microscope with accelerative voltage of 200 kV. Scanning electron microscope (SEM) images were obtained with a Hitachi S-4800 instrument. X-ray diffraction (XRD) was performed with a D/MAX-2400 diffractometer using Cu Kα radiation. Nitrogen sorption isotherms were measured with a Micromeritics TriStar 3000 adsorption analyzer. The gold content was analyzed using an inductively coupled plasma atomic emission spectrometer (ICP-AES) on the Optima 2000 DV.

Results and discussion

Sample properties

First of all, TG-DSC measurement was employed to analyze the thermal behavior of the uncalcined alumina precursors A1-hydro and A2-precip and the corresponding curves are complied in Fig. 1a, b. As expected, A1-hydro shows a different thermal decomposition behavior from A2-precip. The weight loss (~18%) of A1-hydro continues until 450°C which corresponds to the displacement of physically adsorbed water below 100°C, dehydration of aluminum hydroxide and finally transition to γ-alumina. When the temperature exceeds 450°C, no obvious weight loss is observed indicating aluminum hydroxide has transferred to aluminum oxide. Under the same thermal treatment conditions, A2-precip shows a remarkable weight loss (~38%) up to 450°C. Calcination of aluminum hydroxide usually involves the following two reactions [18]:

\[
2\text{A1O(OH)} \rightarrow \text{Al}_2\text{O}_3 + \text{H}_2\text{O} \quad (1)
\]

\[
2\text{Al(OH)}_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \quad (2)
\]

If boehmite or pseudo-boehmite is the primary precipitate, reaction (1) should dominate with a ~15% weight loss accompanied with calcination. If reaction (2) is the primary one, ~34.6% weight loss should be observed after calcination. Based on the above results, we can infer that the as-prepared alumina precursor A1-hydro is mainly composed of AlO(OH) and A2-precip is Al(OH)3.

The DSC curves of A1-hydro and A2-precip (Fig. 1b) display an exothermic peak up to 900°C. However, the height of the exothermic peak of A1-hydro is lower than that of A2-precip, indicating a lower thermal shrinkage and easier phase transition of A1-hydro. Furthermore, A1-hydro and A2-precip were calcined at 500°C in air and then characterized with XRD.

As seen in Fig. 2a, although calcined samples A1-500 and A2-500 can both be assigned to a γ-Al2O3 phase (JCPDS card no. 10-0425), the diffraction peaks of A2-500 are rather weak, indicating a proportion of amorphous phase in the skeleton. The XRD patterns of the gold supported alumina catalysts do not show clear diffraction peaks of the gold nanoparticles, that strongly indicates the deposited gold particles are small in sizes. This is consistent with the TEM observation in Fig. 4. The porosity of the alumina was
characterized using nitrogen sorption at 77 K. As seen in Fig. 2b, the nitrogen sorption isotherms of A1-500 and A2-500 are essentially of type IV. The isotherm of A1-500 has a small continuous nitrogen uptake at $P/P_0=0.2–0.5$, indicating the presence of small mesopores; while the isotherm of A2-500 has a sharp capillary condensation step at $P/P_0=0.8–1.0$, indicative of the presence of larger mesopores, possibly constructed from the closely packed the flake-like alumina. The pore size distributions, determined from the desorption branches of the isotherms by the Barrett–Joyner–Halenda method, show that A1-500 has a narrow mesopore size distribution centered at 2.5 nm, whereas A2-500 shows a rather broad distribution with mesopore sizes concentrated at 3.0 and 35 nm. A2-500 exhibits a higher BET surface area (268 m$^2$ g$^{-1}$) and total pore volume (0.93 m$^3$ g$^{-1}$) than that of A1-500 (222 m$^2$ g$^{-1}$ and 0.34 m$^3$ g$^{-1}$, accordingly). Furthermore, the morphologies of these two samples were characterized by SEM. Hydrothermally synthesized A1-500 shows distinct flake-like features (Fig. 2c); while A2-500 prepared using a precipitation method has an undefined morphology (Fig. 2d).

Catalytic activity

Alumina A1-500 and A2-500 were used as supports to load gold nanoparticles by a DP method. The obtained catalysts were named as Au-(A1-500) and Au-(A2-500). The actual gold contents by weight were 2.08 wt.% for Au-(A1-500) and 1.89 wt.% for Au-(A2-500), as determined by an ICP-AES technique. Prior to a catalytic test, the catalysts were annealed in air at 250°C and 700°C, respectively, and the corresponding catalysts were denoted Au-(A1-500)-250, Au-(A2-500)-250, Au-(A1-500)-700 and Au-(A2-500)-700. As shown in Fig. 3, catalyst Au-(A1-500)-250 shows a high activity and 1% CO can be completely oxidized to CO$_2$ at 10°C, which is a significantly higher activity as compared to most reported Au/Al$_2$O$_3$ catalysts [12, 19]. The TEM image (Fig. 4a) shows that gold nanoparticles in sample Au-
(A1-500)-250 are highly dispersed and an average particle size of \(\sim 1.8\) nm is determined from TEM images by measuring a minimum of 200 gold particles. The small gold particle size and high activity of the catalyst for CO oxidation confirmed the finding of Häkkinen’s work [4]. In the case of Au-(A2-500)-250 catalyst, the temperature of complete CO conversion (\(T_{100\%}\)) rises sharply up to 100°C (see Fig. 3). In addition, based on the results from Fig. 3, the estimated reaction rates (listed in Table 1) indicate that the flake-like alumina is an active catalyst support. As shown by the TEM image in Fig. 4a, many gold particles of \(\sim 3\) nm size are present, which are larger than those \(\sim 1.8\) nm of Au-(A1-500)-250. In addition, some even larger gold nanoparticles with sizes \(\sim 10\) nm are also observed. It is common that gold tends to form large particles \(\sim 7\) nm in size. This reveals that the gold nanoparticles must be trapped/stabilized by the alumina support, which can be related to its unique flake-like morphology. By carefully comparing the TEM images in Fig. 4, it can be seen that the surfaces of thin flakes on the A1-500 support are very rough.

To date, in the absence of an additional promoter (e.g., CeO\(_2\)) for the support, active Au/Al\(_2\)O\(_3\) catalyst with high-temperature resisting was hardly found. This is due to the low Tammann temperature of gold nanoparticles which generally tend to melt and sinter at high temperature. Surprisingly, in our case, the catalyst Au-(A1-500)-700 calcined at 700°C shows a high activity and the complete conversion of CO can be achieved at a temperature as low as 30°C (Fig. 3). In contrast, the catalyst Au-(A2-500)-700, synthesized using the common precipitation method shows no activity (Fig. 3). This experiment was repeated three times and identical results confirmed the reproducibility. According to the literature and our present results, we preliminarily attributed the flake-like alumina support play an important role in stabilizing the gold nanoparticles during high-temperature annealing. To understand that, we therefore further characterized this catalyst using TEM. As shown by the TEM image in Fig. 4, the TEM image shows that the diameter of the gold nanoparticles in sample Au-(A1-500)-700 is \(\sim 2.2\) nm in size. This reveals that the gold nanoparticles must be trapped/stabilized by the alumina support, which can be related to its unique flake-like morphology. By carefully comparing the TEM images in Fig. 4, it can be seen that the surfaces of thin flakes on the A1-500 support are very rough.

Table 1 Estimated reaction rates

| Sample         | Au (at.%) | T(K) | Rate (mol h\(^{-1}\) g\(_{Au}\)^{−1}) | TOF(s\(^{-1}\))\(^a\)^b |
|----------------|-----------|------|--------------------------------------|---------------------------|
| Au-(A1-500)-700| 2.08      | 293  | 1.508                                | 0.0825                    |
| Au-(A2-500)-700| 1.89      | 293  | 0.053                                | 0.0029                    |
| Au-(A1-500)-250| 2.08      | 293  | 1.604                                | 0.0878                    |
| Au-(A2-500)-250| 1.89      | 293  | 0.884                                | 0.0484                    |

\(^a\)Turnover frequency was calculated based on the number of the supported Au atoms

\(^b\) The value of TOF in literature[24, 25] is \(<0.009\) s\(^{-1}\)
and contain numerous small and surface orientated mesopores. The presence of small mesopores has been confirmed by the aforementioned nitrogen sorption measurement. These shallow small mesopores should act as containers which prevent the gold nanoparticles from escaping and sintering, and thus enabling an excellent activity and thermostability. In contrast, the TEM image of Au-(A2-500)-700 (Fig. 4d) shows significant sintering of gold nanoparticles with sizes greater than 20 nm after thermal annealing at 700°C. Theoretically, to form one spherical particle with a diameter of 20 nm would require the merging of 1,000 particles with a diameter of 2 nm. It is clear that the sintering of gold particles is responsible for the complete loss of CO oxidation activity [5]. Hence, we proposed that the unique structure of such thin flake alumina A1-500 with numerous small mesopores may provide structural defects and cavity (see the scheme illustration in Fig. 4), which hinder the mobility and sintering of the supported gold nanoparticles [21, 22]. This in principle is similar to the previous finding that Pt nanoparticles can be stabilized on carbon supports with rough surface and cavities [23].

Conclusions

It has been discovered that hydrothermally synthesized flake-like alumina is able to stabilize gold nanoparticles with small sizes (predominantly ~2.2 nm) and high dispersion, even after annealing of the catalyst to 700°C. The high activity of such a catalyst was proven using the model CO oxidation reaction as evidenced by a complete conversion of CO at 30°C. The very rough surface and numerous small mesopores on this alumina support were found to be responsible for the stabilization of the gold nanoparticles. Such an alumina could be an ideal candidate for the preparation of high temperature stable catalysts, e.g., catalyst for the water gas shift reaction.

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