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**SYNTHESIS OF METAL-DOPED TiO₂ NANOTUBES AND THEIR
CATALYTIC PERFORMANCE FOR LOW-TEMPERATURE CO
OXIDATION**

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Abstract

Gold-, gold and copper-doped TiO₂ nanotubes (Au/TiO₂ NTs, Au-Cu/TiO₂ NTs) are prepared by impregnation-reduction method. The doped nanotubes are characterized by powder X-ray diffraction (XRD) and transmission electron microscopy (TEM). Their catalytic performance for CO oxidation is also examined.

Keywords: Doped TiO₂ nanotubes, gold, copper, CO oxidation

INTRODUCTION

Low-temperature CO oxidation is of great use in various fields, e.g. elimination of CO from automobile emissions, CO gas sensors, gas purification in the laser, and air-purification devices for respiratory protection [1-3]. Following the discovery that gold nanoparticles supported on metal oxides are very active for low-temperature CO oxidation, many different kinds of catalysts

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have been developed [3-6]. Among them, Au-TiO₂ system has been intensively researched [3-5]. As a general rule, a suitable support is crucial to their functional performances [7]. Because TiO₂ nanotubes have large surface area, they should be better supports than TiO₂ powder for preparation of TiO₂ supported catalysts. In 1998, Kasuga developed a simple hydrothermal process to prepare TiO₂ nanotubes of high quality [8]. Since then, the modification of TiO₂ nanotubes by gold has been becoming an attractive field [9-11]. Tomoki Akita has prepared Au/TiO₂ NTs by deposition-precipitation method, but catalytic activity of the doped nanotubes for CO oxidation is relatively low [11]. In this letter, impregnation-reduction method is used to prepare Au/TiO₂ NTs. Their catalytic activity for CO oxidation is also studied. In order to improve the catalytic activity and reduce gold content of Au/TiO₂ NTs, copper is added during the fabrication process.

EXPERIMENTAL

Preparation of catalysts

All of the chemicals are analytical grade and used without further purification. Water is of ~18 MΩ·cm resistivity.

Preparation of TiO₂ nanotubes

TiO₂ nanotubes are synthesized in a manner similar to that Kasuga reported [9]. Pure anatase TiO₂ powder is dispersed in an aqueous solution of NaOH (10 M) and charged into a Teflon-lined autoclave. The autoclave is heated in an oil bath at 150°C for 12 h. Prepared sample is washed with 0.1 M HCl solution and water, respectively. White TiO₂ nanotubes are obtained after they are dried at 80°C in air.

Preparation of Au/TiO₂ NTs

The TiO₂ nanotubes are dispersed in water before appropriate volume of HAuCl₄ solution (0.21 mg/mL) is added. The solution is adjusted to pH = 7 with NH₃ and stirred for 1 h. The suspension is centrifuged and washed with water to remove Cl⁻ ions. After dried at 80 °C overnight, the precipitation is reduced in hydrogen at 150°C for 2 h. The calculated gold content is 1 wt.%, 0.5 wt.%, and 0.1 wt. % (denoted as Sample A, B and C), respectively.

Preparation of Au-Cu/TiO₂ NTs

TiO₂ nanotubes are dispersed in water before Cu(NO₃)₂ solution is poured into it. After water is removed completely at 100°C under stirring, the impregnated TiO₂ nanotubes are calcined at 300°C for 3 h to obtain CuO doped TiO₂ nanotubes (CuO/TiO₂ NTs). CuO/TiO₂ NTs instead of TiO₂ nanotubes is used to synthesize Au-Cu/TiO₂ NTs (denoted as Sample D) by the same process as b. The calculated gold and copper contents are 0.1 wt.% and 8 wt.%, respectively.

Catalyst characterization

The powder X-ray diffraction (XRD) is carried out at room temperature using a Rigaku D/Max-2500 X-ray diffractometer (CuK α λ = 0.154 nm) to determine the crystal structure of the products. Diffraction peaks of crystalline phases are compared with those reported in the JCPDS Data File. TEM images are obtained with a Philips T20ST transmission electron microscopy working at 200 kV.

Catalytic test

Catalytic tests of the catalysts for CO oxidation are carried out in a fixed-bed flow microreactor (7 mm i.d.) under atmospheric pressure using 100 mg catalyst powder. Reaction gas mixture consisting of 1% CO balanced with air is passed through the catalyst bed at a total flow rate of 33.6 mL/min. The composition of reactant and product is analyzed on-line with a GC-508A gas chromatograph equipped with a thermal conductivity detector (TCD). T_{100%}, which is an important parameter for evaluating catalysts' performance, is the temperature for 100% CO conversion on catalyst.

RESULTS AND DISCUSSION

Microstructural characterization of the doped TiO₂ nanotubes

Figure 1 depicts the typical XRD patterns of Au/TiO₂ NTs with different gold content and Au-Cu/TiO₂ NTs. Diffractions that are attributable to anatase phase of TiO₂ are clearly detectable in all samples (JCPDS 21-1272). Peak at $2\theta = 44^\circ$ in Sample A is designated as reflection of gold (2 0 0) (JCPDS 4-0784), which proves that TiO₂ nanotubes are doped by gold particles. However, no

obvious gold peak is found in Sample B, C and D. It is probably due to the low gold content and high dispersion of gold on TiO₂ nanotubes. New peaks at $2\theta = 43^\circ$ and 50° emerge in Sample D corresponding well to (1 1 1) and (2 0 0) reflections of copper (JCPDS 4-836) respectively, which proves that copper particles exist in Sample D.

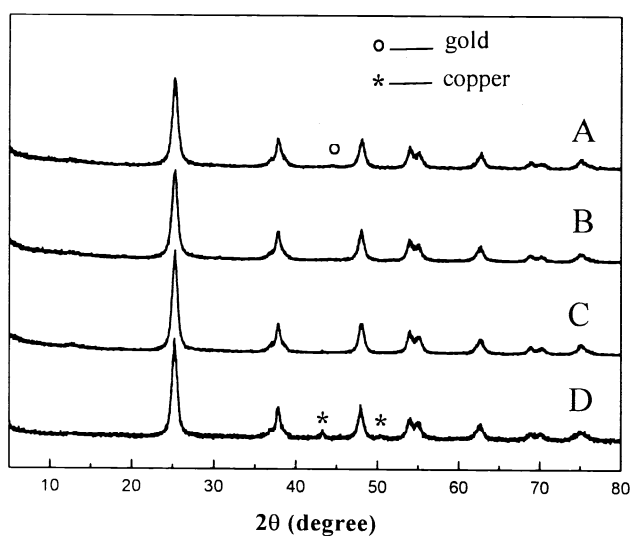


Fig. 1. XRD patterns of Sample A, B, C and D

TEM images of Au/TiO₂ NTs

A deep insight into the nanostructure of Au/TiO₂ NTs can be obtained by TEM observations. Figure 2 displays typical TEM images of Sample A and C. As shown in Fig. 2A, the gold particles are supported on TiO₂ nanotubes or at the interface between bundles of nanotubes. At higher magnification (Fig. 2B), a careful examination of the doped nanotubes reveals that gold nanoparticles are both encapsulated in (marked with arrows) and deposited on the nanotubes. The TiO₂ nanotubes are impregnated with HAuCl₄ solution during the impregnation process. Further reduction treatment induces formation and growth of gold particles within the tubes, which is responsible for the result of Fig. 2B. Average size of the gold particles is about 10 nm. And the gold content does not influence the size of gold particles apparently, which can be concluded from Fig. 2C.

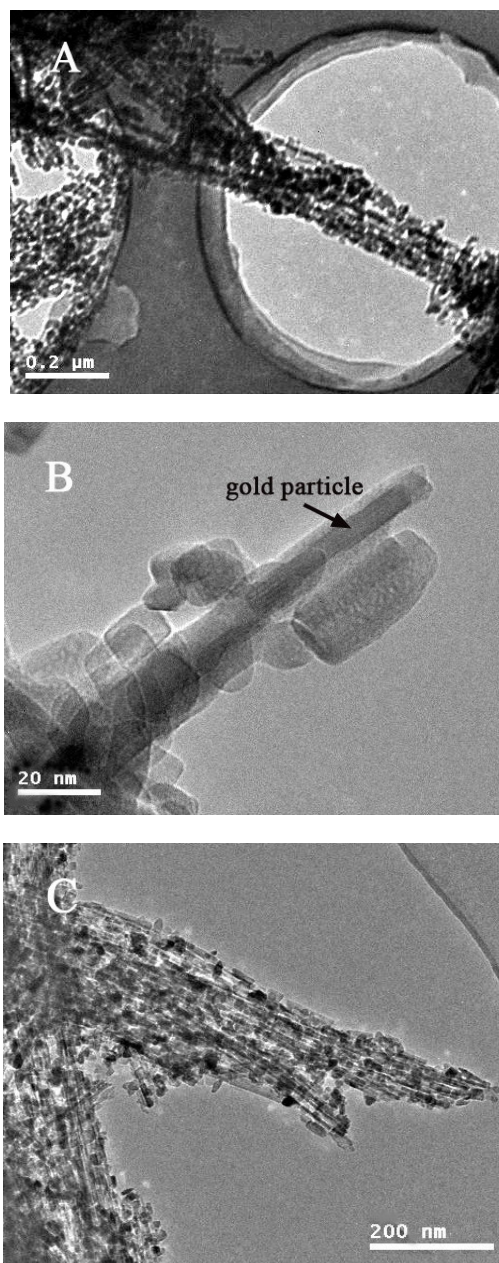


Fig. 2. TEM images of (A, B) Sample A and (C) Sample C

Catalytic activities of the doped TiO₂ nanotubes

Figure 3 presents the catalytic activities of Sample B and C *vs* reaction temperature. It is noted that the CO conversion increases with the raise of reaction temperature under the present reaction conditions. Table 1 shows the comparison of catalytic activities of all samples for CO oxidation. For Sample A, absolute conversion can be obtained below room temperature. The light-off temperatures for 100% CO conversion on Sample B and C are 60°C and 170°C, respectively. Obviously, CO conversion increased with increasing gold content. As has been monitored, pure TiO₂ nanotubes exhibit no activity under the same conditions, which indicates that gold particles are active centers of Au/TiO₂ NTs. After copper is added, catalytic activity of the supported gold increases obviously. The light-off temperatures for 100% CO conversion on Sample D is 70°C, which is 100°C lower than Sample C and is close to the activity of Sample B. There should be a synergistic interaction between gold and copper, which is responsible for the high activity.

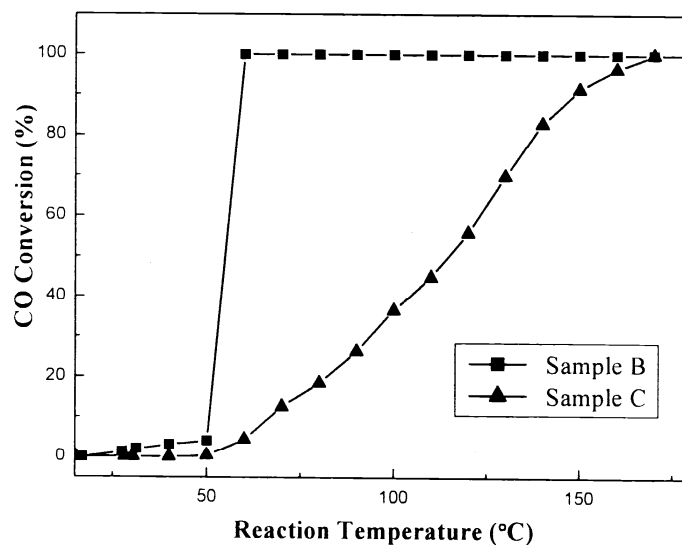


Fig. 3. Catalytic activities of Sample B and C *vs* temperature

Table 1
Catalytic activities of Sample A, B, C and D for CO oxidation

Sample	A	B	C	D
T _{100%}	Below room temperature	60°C	170°C	70°C

As discussed above, Au/TiO₂ NTs with high catalytic activity for CO oxidation are prepared by impregnation-reduction method. Bollinger has reported that impregnated catalysts must in fact undergo hydrogen reduction for high activity and are deactivated by calcinations [12]. So reduction treatment should be a crucial process for the synthesis of Au/TiO₂ NTs with high catalytic activity. Tomoki Akita has prepared Au/TiO₂ NTs by deposition-precipitation method [11]. But the doped nanotubes have low activity for CO oxidation [11]. That should be attributed to the calcination treatment during fabrication process.

The CO oxidation activities of Sample A and D as a function of reaction time are also monitored. Activities of the catalysts do not decay over 10 h in the present study, which indicates the high stability of prepared catalysts.

CONCLUSIONS

In this work, Au/TiO₂ NTs and Au-Cu/TiO₂ NTs are fabricated by impregnation-reduction method. The TiO₂ nanotubes supported catalysts have a constant and high activity for CO oxidation. This is a significant attempt for TiO₂ nanotubes as catalyst carriers. After copper is added, the activity of supported catalyst is enhanced obviously. This is somewhat surprising in the view of low gold content.

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