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Synthesis of Au–CeO_2/SiO_2 catalyst via adsorbed-layer reactor technique combined with alcohol-thermal treatment

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ABSTRACT

Au–CeO_2/SiO_2 was prepared via adsorbed-layer reactor technique combined with alcohol-thermal treatment. The catalytic performance in complete oxidation of benzene was investigated. TEM, Raman characterization showed that Au particles grew up obviously during alcohol-thermal process, while CeO_2 particles maintained 4 nm in diameter. The content of oxygen vacancies and adsorbed oxygen species on catalysts surface increased apparently. Alcohol-thermally treated Au–CeO_2/SiO_2 and CeO_2/SiO_2 showed similar change in catalytic performance, and were much superior to calcined CeO_2/SiO_2. Of alcohol-thermally treated and calcined CeO_2/SiO_2, initial temperatures of the reaction were 80 °C and 150 °C, respectively. The benzene conversions reached 85% and 40% at 300 °C.

1. Introduction

The research on the catalytic features of supported gold catalyst in the reactions, such as CO oxidation [1,2], combustion of VOCs [3], and selective hydrogenation of acrolein [4] have gained more attention over the last decades. At present, the characteristics of gold, such as size [5,6], mole ratio of $Au^{\delta+}/Au^0$ [7,8], geometrical configuration [9], attracted most researchers' attentions. Usually, those were regulated by changing the component [10,11] or structure [12,13] of the support. However, the support was found not just regulate gold microstructure, but also participate in catalytic cycle. Volpe [14] and Yin [15] suggested that the nature of gold decided the activity in selective hydrogenation of crotonaldehyde and epoxidation of styrene, respectively, while Milone et al. [4] believed that was the nature of support, in selective hydrogenation of α–β unsaturated aldehyde. The support or gold, which one had the decisive role was still controversial. The difficulty was that the regulation of gold and the support was interdependent, making the judgment that which was the main cause for the alteration in catalytic features inaccuracy. In this predicament, we carry out an exploratory research by employing a new method, named Adsorbed-layer reactor technique (ALRT), combining alcohol-thermal treatment, trying to decouple these two processes.

Because of its favorable redox properties and oxygen storage capacity, CeO_2 was usually used as supporter or auxiliary component in Au catalysts [16,17]. Some studies confirmed that by employing nanocrystalline or mesoporous CeO_2, the catalytic activity increased apparently, even two orders of magnitude [18]. It was probably because of the stronger metal–oxide interaction [19] and satisfactory oxygen vacancy content [20]. It suggested that the properties of ceria might dominate in this system. Herein, we chose Au–CeO_2 as a typical system, trying to find out which one had the decisive role, typically in benzene complete oxidation, CeO_2 or gold?

2. Experimental methods

2.1. Materials

Hydrophilic silica (SiO_2; Degussa AEROSIL200, average size 12 nm, specific area 200 m^2/g), Ethanol (C_2H_5OH; AR, Hangzhou Xiaoshan Chemical Reagent Ltd.), Cerium nitrate ($Ce(NO_3)_2{\cdot}6H_2O$; AR, Sinopharm Chemical Reagent Co., Ltd.), Sodium hydroxide (NaOH; AR, Hangzhou Chemical Reagent Ltd.), Gold(III) chloride ($HAuCl_4{\cdot}4H_2O$; AR, Shanghai Chemical Reagent Co., Ltd.), Soldium borohydride ($NaBH_4$; AR, Sinopharm Chemical Reagent (Shanghai) Co., Ltd.), Benzene (C_6H_6; AR, Sinopharm Chemical Reagent (Shanghai) Co., Ltd.).

2.2. Synthesis process

The synthesis method of the catalysts was similar as that in Jiang et al. [21], using $Ce(OH)_3$ as modification component. The

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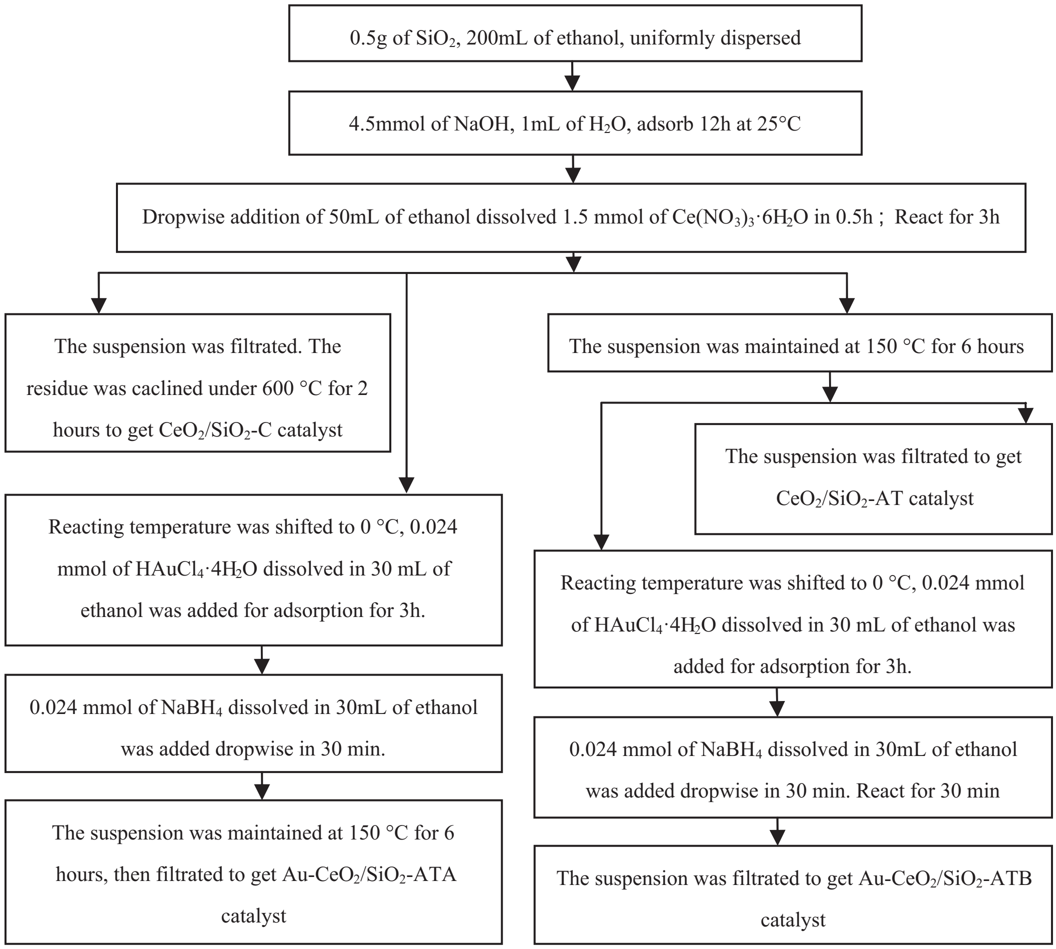

Fig. 1. Preparation process of the catalysts.

preparation processes were under stirred condition and showed in Fig. 1.

2.3. Catalyst characterization

(A) Transmission Electron Microscopy (TEM): One drop of an ultrasono-mixed, dilute alcohol suspension of the "as-prepared" sample was placed on a carbon-coated grid, and after evaporation of the solvent electron micrographs of the particles retained were taken. A JEM-1230 transmission elector microscope was used.
(B) Raman spectra: The Raman spectra were recorded using a LabRamHRUV double spectrometer with a photomultiplier, operating in the photon counting mode. The 514 nm line of an Ar^+ ion laser was used for excitation. The laser power on the samples was 10 mW. The spectral slit width was 1 cm^{-1}.
(C) X-ray diffraction (XRD): The catalysts were analyzed by XRD using a D/max-rA XRD instrument (XD-98, Philips, Eindhoven, The Netherlands) with Cu Kα radiation (1.5406 Å). The accelerating voltage and the applied current were 40 kV and 30 mA, respectively.
(D) Inductively coupled plasma mass spectrometry (ICP-MS): The content of residual element (Au or Ce) in the solution after synthesis processes was analyzed by ICP-MS instrument (XSENIES, Thermo Fisher Scientific, America).

2.4. Catalysis activity measurements

Complete oxidation of benzene was performed at atmospheric pressure in an up-flow tubular reactor (i.d. 4 mm) made of stainless steel, loaded typically with 0.1 g of powder catalyst diluted with 1.5 g of quartz sand in 40–60 mesh.

For catalytic activity evaluation, a mixture of 2.5 vol% of benzene and air flowing at 80 mL min^{-1} (total WHSV = 48,000 mL $g_{cat}{}^{-1}$ h^{-1}) was admitted and the temperature was raised from room temperature to 650 °C in steps of 25 °C. The concentration of benzene in the inlet and outlet were analyzed by on-line GC (model 1102 by ShangFeng) equipped with a FID detector. No organic byproducts were detected in the outlet, indicating that benzene was deep oxidized.

3. Results and discussion

3.1. Catalysts characterization

ICP-MS analysis showed that less than 0.01% of Au and 0.25% of Ce remained in the filter liquor, demonstrating that almost all of them were loaded on silica.

The morphology of the catalyst was analyzed by TEM. Fig. 2a and b shows TEM pictures of alcohol-thermally treated CeO_2/SiO_2 (named CeO_2/SiO_2-AT) and calcined CeO_2/SiO_2 (named CeO_2/SiO_2-C), respectively. CeO_2/SiO_2-C catalyst was prepared for comparison.