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Promoter effect of La_2O_3 on gold catalyst with different textural structures

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ABSTRACT

Silica supported gold nanoparticles were synthesized and promoted by lanthanum oxide as dopant. The influences of La_2O_3 and silica textural structure on the gold dispersion, formation of active species, crystalline composition and the reacting role of dopants were studied in detail. The characterization results suggested that the dispersion of gold nanoparticles depended on the textural structure of silica without lanthanum oxide doping where small mesopores are more preferable to disperse gold nanoparticles. The addition of lanthanum oxide largely increased the dispersion of gold nanoparticles and oxygen active sites independent of the textural structure of silica support. The interaction between lanthanum oxide and silica enhanced by the synergy facilitated the release of oxygen vacancies and transition of active oxygen species. In addition, the chemical properties were greatly changed after lanthanum oxide addition which was only inconspicuously impacted by the initial textural structure of silica supports, shedding light on the further design of economic gold catalyst based on simple synthesis method.

1. Introduction

The extraordinary catalytic activity of gold catalysts has been reported so far until now for many reactions including the VOC total oxidation, preferential oxidation (PROX) of CO in H_2, water gas shift reaction, reduction of NO to N_2, epoxidation of propene, CO oxidation and so on [1–4]. Large number of works have been done concerning highly active gold catalysts for diverse reactions, however the expensive cost of materials and the easy deactivation of gold catalysts under reaction conditions largely limit the further application of supported gold nanoparticles, which might be caused by particles sintering, carbon deposition, vestigial chloride, active species variation or being covered during reaction and so on [5–7]. The interface perimeter and strong interaction between finely dispersed gold nanoparticles (<5 nm) and support was claimed to be essential for getting efficient gold catalysts [8,9], which were considered as the premium and fundamental theory for promoting methods for gold catalysts.

In order to enhance the catalytic performances of gold catalysts and remit the extravagant processes during synthesis, dopants for optimizing targeted catalysts have attracted considerable industrial and academic interests, particularly for gold nanoparticles supported on inert supports such as alumina and silica [10–13]. It was well demonstrated that the transformation of oxygen species to gold nanoparticles played primary role for the performance of gold catalyst especially for gold nanoparticles supported on silica where gold-silica interaction is quite week and the endow of oxygen species of silica to gold is blocking-up [11,14,15].

The idea of introducing additional metal oxides roots in the fact that the additional metal oxide acts as a role of connector between gold and silica and facilitates the transformation of active oxygen species. Peza-Ledesma et al. [16] took insight into the impact of TiO_2 doping amount based on the SBA-15 supported gold nanoparticles, and found that threshold value existed where 10 wt% TiO_2 doping was preferable. They attributed the high efficiency of gold catalyst to the higher dispersion of particles and generation of positively charged gold species. However the gold catalysts with "most proper" amount of titania doping displayed recessive performance far from the pure Au/TiO_2, which seemed superfluous to make such synthesis and uneconomical to be industrially applied. The study furnished by Xu et al. [17] provided insight into copper doped gold catalyst, which could protect gold species from reduced and inhibit coking and contribute to the high activity for acetylene hydrochlorination at extremely low gold loading (0.2 wt%).

Lanthanum oxide was applied as structural and thermal stabilizer due to its intrinsic basic nature that could improve sintering resistance and particle dispersion [18]. Borer and Prins

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[19] also concluded that addition of lanthanum oxide influenced the surface interaction with the adsorbates leading to improved oxygen-sorption kinetics and increased hydrogen availability at the catalyst interface by lanthanum as dopant for Rh/SiO_2 catalyst during selective CO hydrogenation to methanol.

The textural properties of supports and catalysts played important role for the performances of gold catalysts for various reactions. Gao et al. [20] suggested that the surface area of La_2O_3 promoted SiO_2 incrementally changed with the amount of lanthanum oxide varying from 5–30 wt%. It was also announced that the support with smaller grain sizes and higher surface area is beneficial for the dispersion of active sites which would get higher catalytic activity for structure-sensitive reactions [21]. However it seemed not to be the case in Gao's work since there was no evidence of any correlation of the surface area and the CH_4 conversion and the addition amount of La_2O_3 was quite high. It can be summarized that there is still no clear and convinced declaration concerning the real function roles despite the differences of intrinsic factors of the catalyst such as the textural parameters and the synergy between active sites and support. What the real role of dopant is during CO oxidation, what they do promote during the synthesis processes and the reaction, will it perform as chemical promoter or textural promoter or even both?

In this work, three kinds of silica with distinctive textures will be used as support of gold nanoparticles. The chosen of silica as carrier is based on the consideration that the interaction between Au–silica is weak in all the three cases despite the distinctive textures of silica which makes the understanding of dopants more simplified. Lanthanum was applied as typical dopants to understand the function roles of dopant both on performance, chemical and textural properties under with distinctive-texture-samples as catalyst models.

2. Experimental

2.1. Synthesis of catalyst

The La_2O_3 promoted silica with different porous properties were synthesized by impregnation method. The synthesis processes are similar as the previous work [22,23]. Three kinds of silica (Qingdao Hangyang Chemical Plant) with different textural properties were applied as initial support and modified by lanthanum oxide, respectively. 1 g of silica and lanthanum oxide was added into a 100 mL baker consequently under vigorous stirring. The weight ratio of La_2O_3/SiO_2 in all samples was kept at 6 wt%. The samples were dried at 383 K in the oven overnight, labeled as La_2O_3/Si-1, La_2O_3/Si-2 and La_2O_3/Si-2 for different silicas as initial support. The gold catalysts (gold loading of 1.5 wt% to silica) were prepared by the deposition–precipitation method using NaOH as precipitator. The $HAuCl_4{\bullet}4H_2O$ (Sinopharm Chemical Reagent Co. Ltd; Au content 47.8%) was utilized as the precursor. The $HAuCl_4{\bullet}4H_2O$ aqueous solution and the precipitator were slowly co-added into a bottle containing silica or lanthanum oxide modified silica, with the pH controlled between 8 and 9. After filtration and washing, the resulting powder was dried at 333 K for 24 h, followed by calcination at 533 K for 4 h. The related samples were marked as Au/La_2O_3/Si-*n* and Au/Si-*n* (*n* related with the number of type of silica), respectively.

2.2. Characterization of catalyst

The BET surface area and pore volume were measured on a NOVA1000e instrument of Quantachrome Company [24]. The phase purity of the sample was confirmed by X-ray diffraction (XRD) measurement. It was performed with an MPD type X'pert powder diffractometer equipped with Cu-$K\alpha$ (λ = 1.54056 Å) radiation, which was operated at 40 kV and 30 mA for 2θ angles ranging from 10° to 80°. The particle sizes were calculated by Scherrer's equation. TEM measurement was performed on the JEOL-JEM-200CX transmission electron microscopy. X-ray photoelectron spectroscopy (XPS) experiments were performed on the XSAM 800 spectrometer with an Al anode for $K\alpha$ (1486.6 eV) radiation. The binding energies in XPS spectra were referenced with respect to the C 1 s binding energy of adventitious carbon in the catalysts at 285.1 eV. The steps of O_2-temperature-programmed desorption (O_2-TPD) were similar with our previous work [25], 200 mg of fresh catalyst was loaded, and adsorbed in O_2 at 300 °C for 60 min. After the powder was cooled to 50 °C, it was blown by N_2 for 120 min. The catalyst was then heated to 750 °C at a linear heating rate of 10 °C/min in the N_2 flow. The effluent gas was analyzed with a mass spectrometer.

2.3. CO oxidation

The catalytic performance was evaluated with a fixed-bed flow reactor. 100 mg sample powder was used as catalyst. The reactant consisting of 1% CO and 21% O_2 and 78% Ar was fed at a rate of 30 mL/min (18,000 mL/(h•g_{cat})). The composition of the effluent gas was detected with an online SC-200 gas chromatograph equipped with a TDX-01 column. The CO conversion was calculated from the change of CO concentration in the inlet and outlet gases.

3. Results and discussion

In order to understand the doping impacts on the performances of gold catalysts based on silica supports with different porous structures, the textural structures of each support are studied by the N_2 adsorption–desorption technique. The N_2 adsorption–desorption isotherm and BJH pore size distribution of different pure silica supports are shown in Fig. 1. Both the isotherms of Si-1 and Si-2 display the isotherm type IV, which possess the hysteresis and are typical characteristic of mesoporous structure according to the IUPAC classification [26], whilst the isotherm of Si-3 shows similar path of adsorption and desorption with an increase at high temperature, corresponding to the isotherm type II.

The silica materials display distinctive porous properties. It can be seen from the BJH pore size distributions that Si-1 and Si-2 are consisted by mesoporous with different pore sizes. Both the micropores (< 2 nm) and macropores (> 50 nm) coexist in the Si-3 silica. The pore size distributions of Si-1 and Si-2 display a sharp peak around 8.4 nm and 18.6 nm respectively, which should be the most probably pore sizes of the two silica materials. The surface areas of three different silica supports are 305.2 m^2/g, 265.3 m^2/g, and 107.9 m^2/g, respectively.

The N_2 adsorption–desorption isotherms of silica and La_2O_3 doped silica with gold loading can be seen in Fig. 1(d–f). It can be seen clearly that the La_2O_3 addition and loading of gold nanoparticles do not obviously change the growing trend of the isotherms and the porous parameters (e.g. surface area and pore volume), suggesting that the mechanical strength of each silica material is strong enough and does not obviously impacted by the doping process. The corresponding BJH pore size distributions of gold supported on both pure silica and La_2O_3 modified silica are also tested for detailed information of silica loaded gold nanoparticles. The pore size distributions after gold loading shift to lower value and more micropores are even generated in the Au/Si-2 and Au/Si-3, suggesting that the gold nanoparticles may fill in the pores and partially cause the collapse of pores of the samples, whereas the doping of La_2O_3 into the catalysts seem not to obviously impact the pore size distribution of samples. In other word it is also suggested that the additional lanthanum oxide with current doping amount is not typical textural promoter.

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