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Silica Modified with Iron(III) Oxide to Support Gold Catalyst for Low-Temperature CO Oxidation

Xiaodong DAI [1, 2] *, **Yuan YAO** [3], **Huanrong LIU** [1]

[1] *Shengli College, China University of Petroleum, Dongying, Shandong, China, 257061*
[2] *Post-doctoral Working Station of University Science Park, China University of Petroleum, Dongying, Shandong, China, 257000*
[3] *Petrochemical Research Institute, CNPC, Beijing, China, 100195*

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Low-temperature oxidation of CO to CO_2 plays a key role in broad application prospects. In order to achieve the low-temperature oxidation of CO, the gold catalyst was prepared using Fe_2O_3-modified SiO_2 as support. The results showed that CO conversion was enhanced over the modified catalyst. At – 10 °C, CO conversion of 95 % could be achieved. The catalysts were characterized by XRD and TEM, and the results showed that the Fe_2O_3 was dispersed in the form of amorphous state. Attributed to the Au-Fe_2O_3 interaction, the modified catalyst exhibited excellent performance for the oxidation of CO.

Keywords: gold catalyst, CO oxidation, SiO_2, Fe_2O_3, interaction.

1. INTRODUCTION

Low-temperature CO oxidation has broad application prospects, such as enclosed CO_2 laser, gas sensors, spacecraft and submarine, CO masks, automotive emissions, hydrogen fuel cells and environmental protections. So, catalysts research for CO catalytic oxidation at low temperature have attracted more and more attentions. In 1987, Haruta [1] reported that nano-gold supported on metal oxide shows excellent catalytic oxidation performance at low temperature. After that, nano-gold used as catalyst for CO oxidation in lots of applications [2 – 7] was widely reported, and it showed great potential for gold as catalysts. Nowadays, gold catalysts with high activity and low loading have been extensively studied [2 – 7]. Meanwhile, people recognized that the factors affecting gold catalysts activity include gold particle size, support properties, the interaction between support and gold. Among them, the gold particle size is considered to be the key factor [3 – 7]. Gold particle size is mainly decided by the support properties and catalyst preparation methods, and therefore, choosing suitable carrier and preparation methods is important to obtain the gold catalysts with high activity.

SiO_2 is widely used as catalyst support because of its good chemical stability, thermal and mechanical stability, and low price. The conventional deposition-precipitation method is a common method to synthesize nano-gold catalysts with hydrogen tetrachloroaurate(III) ($HAuCl_4{\cdot}4H_2O$) as gold precursor, but this method requires that the isoelectric point of support should be higher than 7. Unfortunately, the isoelectric point of SiO_2 is about 2, which is not suitable for nano-gold loading by the deposition precipitation method. When using SiO_2 as support, the gold precursor should be Au complexes, and the nano-gold catalyst is synthesized by grafting such complexes on SiO_2 surface. Notably, this grafting method is complicated, and these Au complexes are more expensive than $HAuCl_4{\cdot}4H_2O$. So, it is necessary to develop a method to prepare nano-gold catalyst supported on SiO_2 with high efficiency.

Recently, Li et al. [8] reported that a mesoporous iron oxide-silica composite with a high silica content was synthesized by hydrothermal method, and another composite with high iron content was obtained by etching part of silica in alkaline solution. Then gold catalysts were loaded onto both composites by a deposition-precipitation method, and used for CO oxidation. Owing to the significant progress in nanosynthesis over the last 20 years, it is possible to synthesize the nanoparticles with uniform size, morphology, and compositions [9]. For example, gold nanoparticles can be easily synthesized in a large scale of about "kilogram" level through the octadecylamine (ODA) method [10]. In our study, commercial SiO_2 was used as initial support, and impregnation-calcination method was used to modify SiO_2 with Fe_2O_3. When Fe_2O_3 content was lower than 10 wt%, it prefers to form amorphous dispersion on SiO_2 surface, characterized by XRD. Firstly, gold nanoparticles (4 – 6 nm) were synthesized through octadecylamine method, and then were supported on the modified support of Fe_2O_3/SiO_2, getting highly dispersed nano-gold catalyst ($Au/Fe_2O_3/SiO_2$). The experimental results showed that the strong interactions between gold and amorphously dispersed Fe_2O_3, presenting excellent CO catalytic oxidation performance at low temperature. When reaction temperature was – 10 °C, the CO conversion reached to 95 %. Experiments at temperature range

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* Corresponding author. Tel.: 86 15553838827; fax: 86 546-7396910.
E mail address: *xiaodongdai1980@163.com* (X. Dai)

of −10 ~ 100 °C, the prepared catalyst could last for 200 hours with stable performance. It could be concluded that the prepared catalyst shows a good catalytic activity and stability, and had a promising application prospective.

2. EXPERIMENTAL

2.1. Materials

Urea (NH_2CONH_2), chloroauric acid tetrahydrate ($HAuCl_4 \cdot 4H_2O$), iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$), and Silica (SiO_2) were provided by the national medicine group chemical reagent limited company, and all of them are analytic grade. Au content of the $HAuCl_4 \cdot 4H_2O$ is 47.8 wt.%.

2.2. Methods

Iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) was dissolved in distilled water with certain volume, and then was supported onto SiO_2 by the initial immersion method. After ultrasonic treatment for 10 minutes, samples were dried at 100 °C for overnight, and then were calcined at 500 – 600 ℃ for 5 hours. Finally, catalyst support of Fe_2O_3/SiO_2 was obtained. According to the reported method [10], gold nanoparticles were synthesized and dispersed in cyclohexane. Fe_2O_3/SiO_2 support was impregnated in cyclohexane solution of gold nanoparticles, and was stirred and evaporated at room temperature to obtain nano-gold catalyst. Catalyst was expressed as Au-x/Fe_2O_3-y/SiO_2 in paper, and "x" and "y" were mass contents of Au and Fe_2O_3, respectively.

2.3. Characterization

The N_2 adsorption/desorption isotherms at −196 ℃ were obtained using a Autosorb-3B porosity analyzer (Quantachrome USA.). Prior to analysis, samples (0.2 g) were degassed at 400 ℃ for 4 h, until the pressure was less than 1 Pa. The specific surface area was deduced by applying a BET equation from isotherm data. The BJH equation was used to determine the mesopore volume and size distribution. X ray diffraction (XRD) was obtained using D8 type Advance (Bruker company, German), with Cu Kα ($\lambda = 0.154$ nm) as radiation source, voltage of 40 kV, current 40 mA, scan rate 0.1 °/min, and scan range 20 – 85°. Surface morphology and particle size of gold nanoparticles were analyzed by transmission electron microscopy (TEM, Japan, JEOL-JEM-2010). Gold content was tested by inductively coupled plasma (ICP-AES) method (Thermo Scient method iCAP 6300 ICP).

2.4. Catalytic testing

0.2 g gold catalyst with 200 – 300 mesh was put into reaction tube (U type), adjusting flow rate of feed gas as required (Fig. 1). Feed gas was consisted of CO with volume content of 1 %, and air of 99 %. Reaction temperature and pressure were set at −10 – 150 °C and 1.013×10^5 Pa respectively. The gas hourly space velocity (GHSV) of 20000 or 30000 mL g^{-1} h^{-1} was used to examine the as-prepared catalysts. Gas chromatography (Shanghai Kechuang chromatograph instrument production company GC9800, N2000 workstation with Zhejiang University Zhida Information Engineering Co. Ltd, Porapak-Q column) was used to measure the content of CO before and after the reaction in the gas mixture.

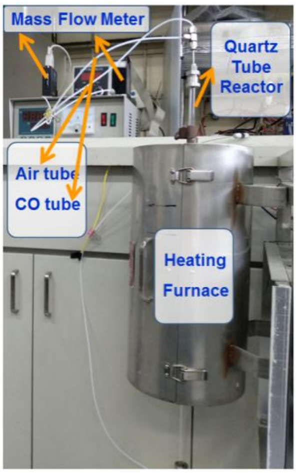
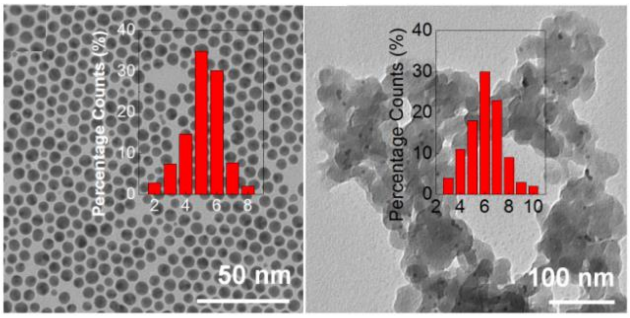


Fig. 1. Experimental set-up for CO oxidation

3. RESULTS AND DISCUSSION

3.1. Synthesis and catalytic performance of pure gold nanoparticles



a b

Fig. 2. TEM images: a – of the Au nanoparticles; b – the catalyst Au-3/SiO_2

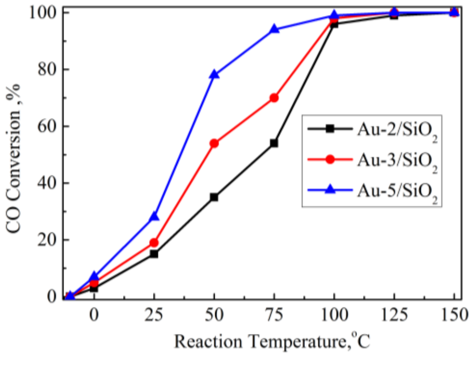


Fig. 3. The performance of the catalyst Au/SiO_2 for CO oxidation. GHSV of 20000 mL g^{-1} h^{-1}

Fig. 2 a shows the TEM image and particle size distribution of the as-synthesized gold nanoparticles [10]. It can be seen that the particle size mainly distributed among 4 – 6 nm. The nano-gold catalyst of Au-3/SiO_2 using pristine SiO_2 as support is presented in Fig. 2 b with almost unchanged Au size of 5 – 7 nm, and it was tested for the CO oxidation reaction. As indicated in Fig. 3, the Au-3/SiO_2 catalyst gave only 20 % CO conversion at 25 °C, which is much lower than the full CO conversion for the reported gold catalysts under similar conditions [3]. With the increase of gold content, the conversion of CO increased gradually. At 50 °C, the CO conversion was 34 % for the Au-2/SiO_2 catalyst, 54 % for the Au-3/SiO_2 catalyst, and 78 % for the Au-3/SiO_2 catalyst. Obviously, it is difficult to obtain the high CO conversion just via raising the gold content. So, it is necessary to modify the SiO_2 support to improve the catalyst performance.

3.2. SiO_2 modification with Fe_2O_3 and its catalytic performance

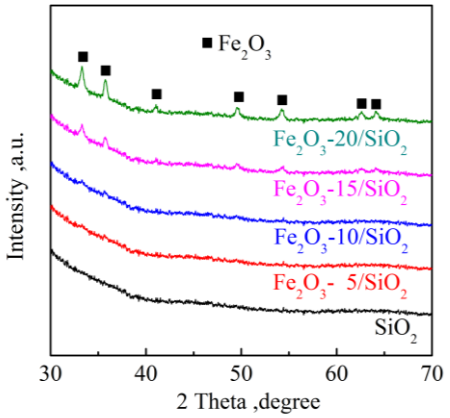


Fig. 4. The XRD patterns of SiO_2 and Fe_2O_3/SiO_2 catalysts with different loadings.

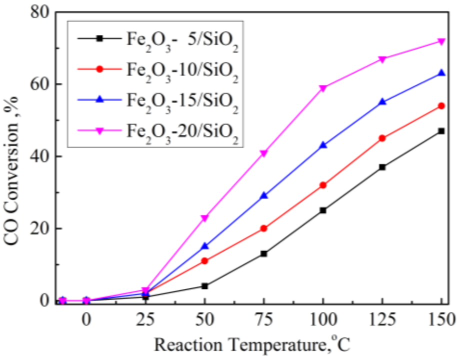


Fig. 5. The performance of the catalyst Fe_2O_3/SiO_2 for CO oxidation. GHSV of 20000 mL g^{-1} h^{-1}

SiO_2 modification with Fe_2O_3 by impregnation-calcination method was studied in this part. XRD pattern shown in Fig. 4, when Fe_2O_3 content is lower than 15 wt.%, there is not characteristic peaks of Fe_2O_3, likely referring to its low weight percentage; while Fe_2O_3 content is higher than 15 wt.%, the α-Fe_2O_3 peaks were observed, indicating that crystal structure is formed. This means that the threshold value for Fe_2O_3 amorphous dispersion is 15 wt.%. Then the catalytic reaction was analyzed, and Fig. 5 shows the performance of the Fe_2O_3/SiO_2 catalyst in CO oxidation. At 50 °C, the Fe_2O_3/SiO_2 sample with 10 wt.% Fe_2O_3 delivers a CO conversion of 15 %, and when Fe_2O_3 content increases to 20 wt.%, CO conversion is just increased to 23 %. These results indicated that it is also very difficult to obtain high CO conversion only by increasing Fe_2O_3 content.

3.3. Preparation of the Au/Fe_2O_3/SiO_2 catalyst and its catalytic performance

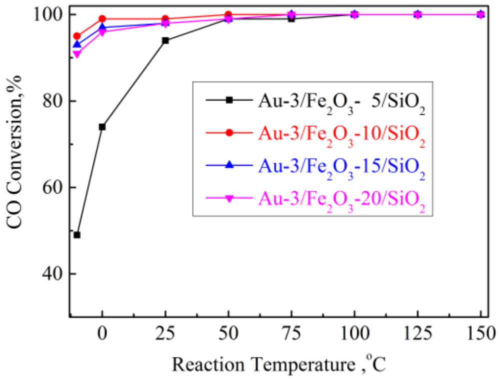


Fig. 6. The influence of Fe_2O_3 loading on the catalytic performance. GHSV of 20000 mL g^{-1} h^{-1}

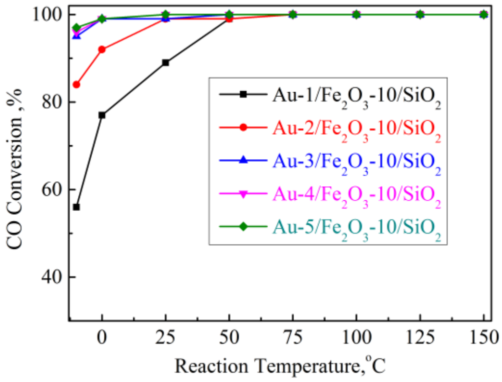


Fig. 6. The influence of gold loading on the catalytic performance. GHSV of 20000 mL g^{-1} h^{-1}

The catalyst performance of Au/Fe_2O_3/SiO_2 with Au content of 3 wt.% is shown in Fig. 6. At 25 °C, the CO conversion increases to 94 % for the Au-3/Fe_2O_3-5/SiO_2 catalyst (with 5 wt.% Fe_2O_3 modification), and then increases to 99 % for the Au-3/Fe_2O_3-10/SiO_2 catalyst (with 10 wt.% Fe_2O_3 modification). After that, with continuous increase of Fe_2O_3 content to 20 wt.%, the CO conversion is reduced to 94 %. Those results indicate that the Au/Fe_2O_3/SiO_2 catalytic activity is greatly reinforced by adding Fe_2O_3. In order to optimize the modification conditions, Fe_2O_3-10/SiO_2 was chosen as support to investigate the influence of Au content. It can be observed in Fig. 6 that, at 25 °C, CO conversion gradually grows up from 88 to 99 %, with gold content from 1 to 3 wt.%.

After that, with gold content increasing, CO conversion could remain at 99 – 100 %. Through the experiments as above, the best modification conditions can be determined to be 10 wt.% Fe_2O_3 and 3 – 5 wt.% gold. Also, catalyst stability of Au-3/Fe_2O_3-10/SiO_2 was investigated at the

GHSV of 20000 and 30000 mL g^{-1} h^{-1}, and illustrated in Fig. 7.

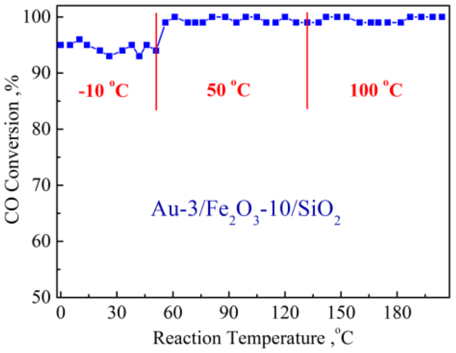


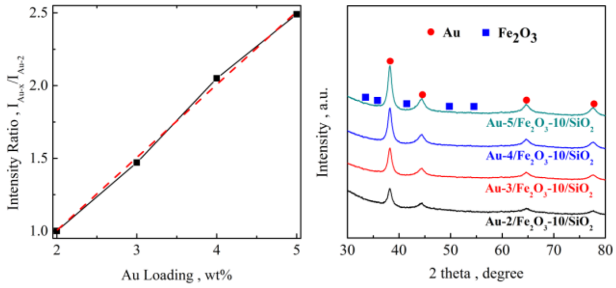
Fig. 7. The stability testing of the Au-3/Fe_2O_3-10/SiO_2 catalyst. GHSV of 20000 and 30000 mL g¯1 h¯1

When reaction temperature was –10 °C and at 20000 mL g^{-1} h^{-1}, CO conversion would stabilize around 93–96 % for 50 h. Then, to investigate the high temperature stability of the as-synthesized catalyst, reaction temperature rises to 50 °C and 100 °C, respectively, and both CO conversions could stay at 99–100 % for 75 h. Particularly, according to the reported method [11], the GHSV is further increased to 30000 mL g^{-1} h^{-1}, and the CO conversion at 50 °C could be stably maintained at 91–93 % for at least 50 h, which indicates good stability for the Fe_2O_3 modified gold catalyst. Furthermore, the CO oxidation was carried out at –10 °C over the 250 h tested catalyst for another 50 h, and the CO conversion is in the range of 93–95 % even after the 70 h testing at 100 °C, indicating a good recoverability of this catalyst. By comparison, the Fe_2O_3 modified catalyst Au-3/Fe_2O_3-10/SiO_2 offers much higher catalytic performance for the CO oxidation than the unmodified counterpart of Au/SiO_2.

3.4. Catalytic mechanism

It is interesting that Au-3/Fe_2O_3-10/SiO_2 catalyst has so high activity for CO oxidation after Fe_2O_3-modification. Some studies have reported that the catalyst structure can be changed during the reaction. For example, the homogeneous nanoalloy of PdZnx was induced into the heterostructure of PdZny@(x-y)ZnO in the real methanol reforming process ($CH_3OH + H_2O = 3H_2 + CO_2$) [12] and Co_3O_4-nanorod supported single-site Pt catalyst was also in situ induced into PtnCom/CoO1-x for the water-gas shift reaction ($CO + H_2O = H_2 + CO_2$) [13]. Moreover, the reference [14] reported that silver nanoparticles supported on MnO remove into the pores of MnO and are transformed into silver monatomic chains during the CH_2O oxidation reaction, which is the reason of the excellent catalytic performance. Consequently, the silver nanoparticles can't be detected by XRD after CH_2O oxidation reaction. We wonder whether the catalyst structure was changed during CO oxidation reaction, which delivers the high CO oxidation activity.

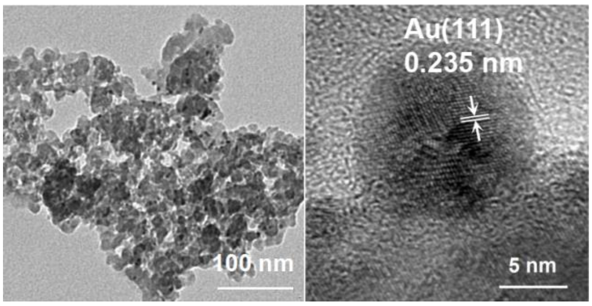
According to the reported method to examine whether the catalyst structure was changed, we also employed XRD to characterize the Au/Fe_2O_3-10/SiO_2 catalysts with gold content of 2 wt.%, 3 wt.%, 4 wt.% and 5 wt.%. Fig. 8 a illustrates that the characteristic peaks of gold did not disappear.



a b

Fig. 8. The XRD patterns: a – of the used Au/Fe_2O_3-10/SiO_2; b – the intensity ratio of Au(111) over these catalysts: Au-2/Fe_2O_3-10/SiO_2;Au-3/Fe_2O_3-10/SiO_2; Au-4/Fe_2O_3-10/SiO2; Au-5/Fe_2O_3-10/SiO_2

In order to display this point more clearly, the Au (111) crystal plane intensity was correlated with gold content. If some gold nanoparticles remove into the Fe_2O_3 and are transformed into gold monatomic chains, the intensity ratios will be different from the ideal intensity ratios. The ideal intensity ratios should be equal to the real gold content ratios for the Au/Fe_2O_3-10/SiO_2 catalysts with gold content of 2 wt.%, 3 wt.%, 4 wt.% and 5 wt.%, which should be 1, 1.5, 2, and 2.5, respectively (with the reference catalyst of Au-2/Fe_2O_3-10/SiO_2). Clearly, the real diffraction intensity ratios of these catalysts are almost equal to their ideal ratios (Fig. 8 b), indicating that the structure of Au nanoparticles did not change during the CO oxidation.



a b

Fig. 9. The images of the used catalyst Au-3/Fe_2O_3-10/SiO_2: a – TEM ; b – HRTEM

Also, gold particle size was investigated after the reaction. TEM image (Fig. 9 a) shows that the average particle size of gold remains at 5–7 nm after reaction, in accordance with gold particle size of the fresh Au/SiO_2 in Fig. 1 b, which implies the particle size of gold didn't change in reaction. Lots of results demonstrate that the strong interaction between gold and oxides could promote catalytic performance in oxidation reactions [4]. Fig. 9 b illustrates the lattice fringes of Au particles, and the Au (111) lattice space is 0.235 nm, which is consistent with the reported results [13]. For Fe_2O_3, its lattice fringe is fuzzy because of its amorphous dispersion. Since the big difference of contrast level between gold and Fe_2O_3, the close contact of each other is clearly observed in Fig. 9 b. Combining the results in sections 3.1.–3.3., it is clear that gold and Fe_2O_3 both had certain catalytic activity for CO oxidation reaction. This is caused by the synergistic effect between gold and Fe_2O_3, which endows the Au-3/Fe_2O_3-10/SiO_2 catalyst with excellent catalytic activity. However, the specific synergistic effect mechanism between them should be further investigated, and the works along this line is in progress.

4. CONCLUSIONS

In our study, gold catalyst supported on Fe_2O_3-modified-SiO_2 presents very good CO oxidation catalytic performance. When reaction temperature is –10 °C, the conversion of CO reaches to 95 %. Fe_2O_3 is amorphously dispersed when its loading is lower than 10 wt.%, and the catalyst with such Fe_2O_3 content possesses good catalytic performance attributed to gold and Fe_2O_3 interface active site. Through Fe_2O_3 modification to SiO_2, it could not only improve the catalytic performance of the catalyst, but also greatly reduce the amount of gold using. In addition, the catalyst shows good stability at different temperatures, which gives good catalyst application prospects.

Acknowledgments

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