Unique Au/α-Fe_2O_3 interfacial structures and their distinct catalytic behaviours in low-temperature CO oxidation and water gas shift reaction

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Abstract: Two α-Fe_2O_3 crystallites of regular morphology (truncated hexagonal bipyramid and quasi cubic) were controllably synthesized. The crystal facets of {113}, {214}, {104}, {110}, and {012} were identified. Au nanoparticles (2.3 nm ± 0.8 nm) were monodispersed on the substrate facets to achieve unique Au/α-Fe_2O_3 interfacial structures and to compare the catalytic behaviours in CO oxidation and WGF reaction. The detailed characterizations clarified the key factors that determined catalytic activities of the two reactions.

Keywords: Gold, Iron oxide, Interfacial catalysis.

1. Introduction

α-Fe_2O_3 is widely used as a reducible substrate with good oxygen storage-release ability. There are α-Fe_2O_3 crystallites of certain morphology synthesized in recent years,[15, 34-39] for the applications of sensing, magnetic property, and catalysis. Few studies, however, have been performed on the interfaces of metal/morphologically uniform Fe_2O_3 substrates. In conventional supported metal catalysts, metal particles of different size are randomly dispersed on various facets, and the observed metal support interaction is the average of many interfacial effects. In the present study, regularly shaped truncated hexagonal bipyramid α-Fe_2O_3 (α-Fe_2O_3-THB) and quasi cubic α-Fe_2O_3 (α-Fe_2O_3-QC) were synthesized as the substrates for precise Au deposition. Special attention has been paid to the effect of unique Au/α-Fe_2O_3 interfacial structures on surface hydroxylation/oxygen adsorption and CO adsorption/activation, accounting for their distinct catalytic behaviours in CO oxidation and water gas shift (WGS) reaction.

2. Experimental

α-Fe_2O_3-THB was synthesized using a $K_4[Fe(CN)_6]\cdot 3H_2O$ solution containing sodium carboxymethyl cellulose, PVP-K30, and hydrazine hydrate. The mixture was hydrothermally treated at 160 °C for 6 h. The solids were washed, dried at 80 °C for 4 h, and air-calcined at 300 °C for 3 h. α-Fe_2O_3-QC was synthesized by changing the relative amount of $K_4[Fe(CN)_6]\cdot 3H_2O$ to hydrazine hydrate. The rest preparation procedures were the same as those adopted for preparation of α-Fe_2O_3-THB. Au/α-Fe_2O_3-THB and Au/α-Fe_2O_3-QC were obtained by controlled deposition-precipitation approach. The nominal Au content is 3 wt% based on α-Fe_2O_3 weight. The samples were characterized by means of XRD, SEM/TEM, O_2(OH)-TPD, FTIR, and CO-TPSR. They were also evaluated in a fixed bed microreactor for CO oxidation and WGS reaction.

3. Results and discussion

The XRD investigation indicated that the substrate crystallites are pure phase in α-Fe_2O_3 form (JCPDS NO. 33-0664). The SEM images (Fig. 1) clearly show the two substrates are morphologically uniform. Through the HRTEM characterization and the inverse fast Fourier transform (IFFT) images as well as the schematic illustrations of structure model of α-Fe_2O_3-THB and α-Fe_2O_3-QC (Fig. 2), it was figured out that in the case of α-Fe_2O_3-THB, four seventh of whole surface belongs to the {113} facets, while two seventh and one seventh of surface belongs to the {214} and {104} facets, respectively. In the case of α-Fe_2O_3-QC, every one third of surface belongs to the {104}, {110}, and {012} facets, respectively. The HRTEM images (Fig. 3a, b) of Au/α-Fe_2O_3-THB and Au/α-Fe_2O_3-QC showed the mean Au particle size is 2.3 ± 0.8 nm and 2.3 ± 0.4 nm respectively. Note that although there are identical facets of {104} over α-Fe_2O_3-THB and α-

Fe_2O_3-QC, in the former case the {104} facet only covers 1/7 of surface while in the latter case it covers 1/3 of surface. The oxygen TPD study indicated that the O_{SL} on α-Fe_2O_3-QC is more reactive (Fig. 4a). Au deposition enhanced oxygen adsorption. However, the variation in O_2-TPD is insufficiently large to account for the deviation in catalytic activities (Fig. 3c). The OH-TPD profiles showed that there are surface OH groups distinctive in reactivity and density on Au/α-Fe_2O_3-THB and Au/α-Fe_2O_3-QC (Fig. 4b). XPS and CO-TPSR studies further demonstrated the function of surface OH/O_L species in reaction.

Complete CO conversion can be accomplished on Au/α-Fe_2O_3-THB even at room temperature, and Au/α-Fe_2O_3-THB certainly outperforms Au/α-Fe_2O_3-QC. Similar situation can be observed for WGS reaction over Au/α-Fe_2O_3-THB and Au/α-Fe_2O_3-QC (Fig. 3d). However, the reaction rates on α-Fe_2O_3-QC are notably higher than that on α-Fe_2O_3-THB. In-situ FTIR study (Fig. 4b) clearly demonstrated that the CO adsorption especially the evolution of surface carbonate intermediates on both the Fe_2O_3 substrates and the Au-loaded samples are considerably different, which should be closely responsible for the significant variation in their catalytic performances.

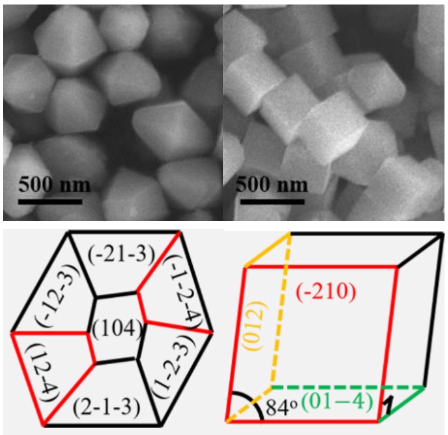

Figure 1. SEM images and schematic diagrams of α-Fe_2O_3-THB (left) and α-Fe_2O_3-QC (right).

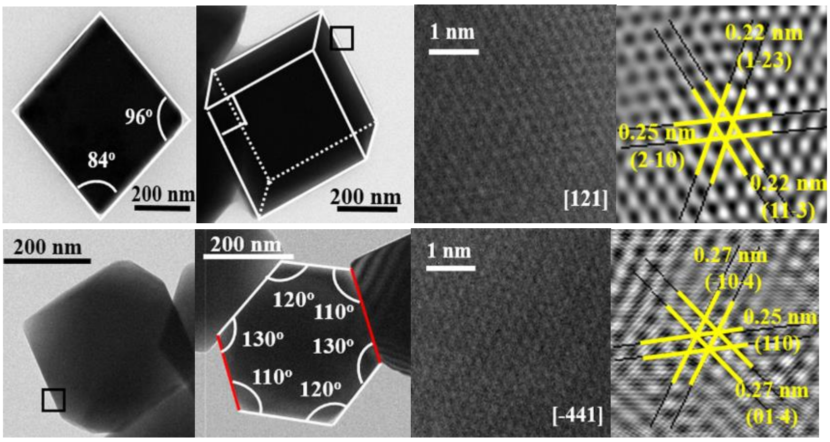

Figure 2. (HR)TEM and IFFT images of Au/α-Fe_2O_3-QC (top) and Au/α-Fe_2O_3-THB (down).

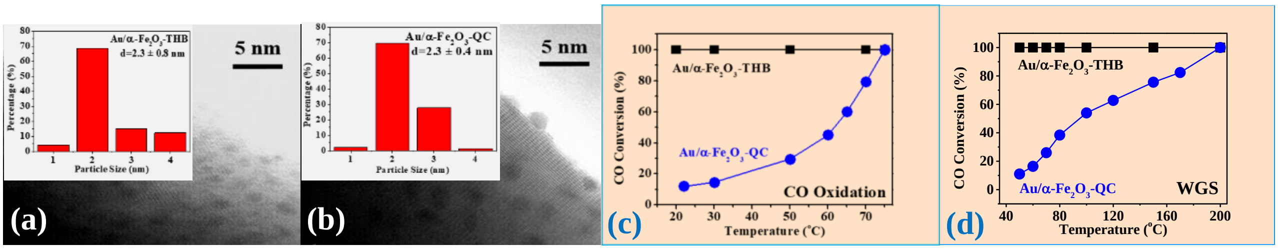

Figure 3. HRTEM images of (a) Au/α-Fe_2O_3-THB and (b) Au/α-Fe_2O_3-QC; CO conversion in (c) CO oxidation and (d) WGS.

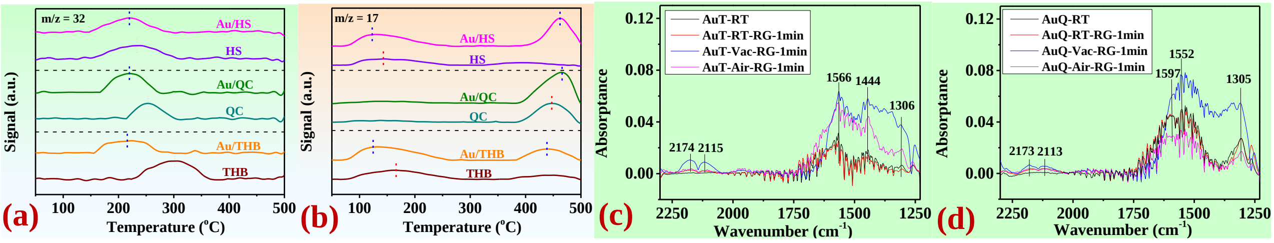

Figure 4. Mass spectra of (a) oxygen and (b) surface hydroxyl TPD as well as FTIR spectra of CO adsorption/reaction over (c) Au/α-Fe_2O_3-THB and (d) Au/α-Fe_2O_3-QC (α-Fe_2O_3-HS and Au/α-Fe_2O_3-HS were employed as reference samples).

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