Low-temperature water gas shift reaction on Cu/SiO_2 prepared by an atomic layer epitaxy technique

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An atomic layer epitaxy technique was used to produce nanoscale 2.9–3.4 nm copper particles supported on silica, and the nanoscale Cu/SiO_2 catalysts can show surprisingly high activity for the water gas shift reaction, in comparison with the 5.6 wt% Pt/SiO_2 and 10.3 wt% Cu/SiO_2 prepared by the impregnation method.

The water gas shift (WGS) reaction ($CO + H_2O \rightarrow H_2 + CO_2$) is used extensively in the conversion of fossil fuels to hydrogen.[1–7] In particular, the WGS reaction achieves the conversion of CO to CO_2, which is important when hydrogen is used as a clean fuel for proton-exchange membrane fuel cells (PEMFC) in view of the strong poisoning effects of CO on Pt-based anodes. Pt-group metals, such as Au or Cu, are suitably used as effective catalysts for WGS reactions because of their high levels of activity and stability.[1–7] However, Pt- and Au-based catalysts can often lead to more activity for WGS reactions than Cu-based catalysts[6,7]. The noble metals are recognized as a scarce resource as well as a limiting step in the development of viable energy alternatives to petroleum. Because of the high cost of precious metals, some transition metals with high levels of catalytic activity for the WGS reaction have been evaluated as alternatives. For example, copper is a potential substitute for noble metals because of its low price and wide use. Thus, if copper-based catalysts can overcome the limitation of low activity, they could prove invaluable.

We have recently used atomic layer epitaxy (ALE) to prepare Cu nanoparticles with average diameters of 2.4 nm on a SiO_2 support.[8] The ALE technique is a surface-controlled, layer-by-layer process that deposits thin films at an atomic scale through self-limiting surface reactions.[9] In our previous study, we showed that ALE-Cu/SiO_2 has very different characteristics from those of typical Cu-based catalysts.[8] In the research reported here, a series of Cu/SiO_2 catalysts with nanoscale copper particles with diameters of 2.9 to 3.4 nm were prepared using the ALE technique at different temperatures. The newly developed copper catalysts were applied to the WGS reaction. In particular, we demonstrate here that low loading of copper can be more effective than the high loading of platinum. If properly developed, nanoscale copper catalysts could be much more economical and may even be able to replace the noble metals for application in WGS reactions.

The ALE-Cu/SiO_2 catalysts were prepared in F-120C ALE equipment (Microchemistry Ltd). The growth experiment was performed in a flow-type reactor at low pressure, with nitrogen as the carrier gas. In each run, 2–3 g of SiO_2 support was used. The SiO_2 support with a surface area of 300 $m^2\ g^{-1}$ used for the ALE sample was purchased from Aldrich Ltd. The SiO_2 support was preheated at 673 K for 16 h to stabilize the number of bonding sites and to remove physisorbed water. The $Cu(thd)_2$ (thd = 2,2,6,6-tetramethyl-3,5-heptane dionate) was introduced at 413 K. $Cu(thd)_2$ was deposited on a SiO_2 support at each of the following temperatures: 433, 443, 453, and 463 K. The reaction time for $Cu(thd)_2$ on the SiO_2 support was 8 h. The IM-Pt/SiO_2 and IM-Cu/SiO_2 samples used in this study were prepared by impregnating the SiO_2 from Aldrich Ltd with an aqueous solution of H_2PtCl_6 and $Cu(NO_3)_2$.

The pretreatments of all ALE-Cu/SiO_2 catalysts used in this study were: (1) calcination at 573 K in air for 5 h; (2) reduction by temperature programmed reduction (TPR) in 10% H_2/N_2 gas from 298 to 973 K after calcination; and (3) reduction at 773 K in H_2 gas for 5 h after TPR reduction. The IM-Pt/SiO_2 sample was calcined in air and reduced in pure H_2 at 673 K for 5 h before use. The IM-Cu/SiO_2 sample was calcined in air and reduced in pure H_2 at 573 K for 5 h before use. High-resolution TEM analysis was carried out on a FEI Tecnai G2 F20 operating at 300 KeV and located at the High Valued Instrument Center at the National Sun Yat-sen University, Taiwan. *In situ* diffuse reflectance infrared Fourier transform (DRIFT) analysis of CO adsorption and CO/H_2O co-adsorption on ALE-Cu/SiO_2 was performed with a Nicolet 5700 FTIR spectrometer fitted with a mercury–cadmium–telluride (MCT) detector operating at 1 cm^{-1} resolution and 256 scans. The DRIFT cell (Harrick Co.) was equipped with ZnSe windows and a heating cartridge that allowed samples to be heated to 773 K. The Pt surface area and dispersion of 5 wt% Pt/SiO_2 used in this paper was measured by H_2 chemisorption at room temperature. The products of pulse reactions for H_2O dissociation and WGS reactions were collected with a quadrupole mass spectrometer (VG Smart IQ^+). All molecules were admitted into the vacuum chamber with helium through a leak valve, at a pressure of about 3.0×10^{-7} mbar. The base pressure in the chamber was typically 2.0×10^{-9} mbar. H_2O was dosed onto the Cu and Pt catalysts by injection through a port located at the upstream of the quartz reactor with a 10 μL Hamilton 7001 syringe. The injection port, similar to that used

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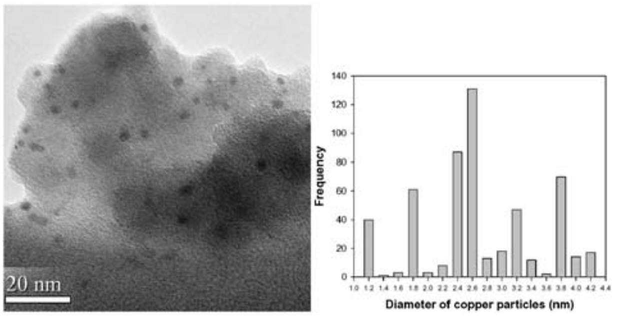

Fig. 1 TEM image and particle size histogram of ALE-Cu-4 catalyst

in gas chromatography, was heated to 373 K to prevent the condensation of water.

We performed TEM experiments on ALE-Cu/SiO_2 synthesized at 463 K to observe the particle size and distribution as shown in Fig. 1. Large amounts of uniform and small nanoscale copper particles were found in the TEM image. The size distribution histograms for the catalyst were obtained by manually measuring the particles from TEM images, as shown in Fig. 1.

Table 1 lists some basic properties of ALE-Cu/SiO_2 catalysts: temperature of the Cu(thd)$_2$ deposited on SiO_2, dispersion, average particle size from TEM images, surface area, number of surface atoms and amount of saturated adsorption of CO. It was seen that the copper content of ALE-Cu/SiO_2 catalysts remained in the range of 2.4–2.8 wt% for preparation temperatures of 433–463 K. The copper particles of ALE-Cu/SiO_2 catalysts had a small mean size and fell between 2.9 and 3.4 nm. The 5.6 wt% IM-Pt/SiO_2 and 10.3 wt% IM-Cu/SiO_2 samples prepared by impregnation methods were also examined for comparison with the ALE-Cu/SiO_2 catalysts.

It was observed that the Pt/SiO_2 catalyst apparently offered a higher CO adsorption amount than all ALE-Cu/SiO_2 catalysts by a factor of 3.9–5.5. The IM-Cu/SiO_2 catalyst showed a similar amount of Cu surface atoms as ALE-Cu/SiO_2, but displayed only very poor CO adsorption.

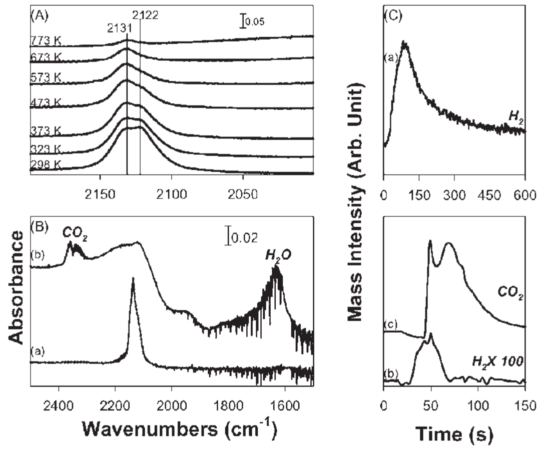

Fig. 2 (A) IR spectra of CO adsorbed on the ALE-Cu-4 catalyst at different temperatures. (B) IR spectra of the co-adsorption of CO and H_2O on ALE-Cu-4 catalyst at 298 K: (a) samples were exposed to a 30 ml min^{-1} pure CO stream at atmospheric pressure for 30 min, followed a 30 ml min^{-1} helium stream to purge the CO gas for 30 min; (b) 5 μl of H_2O were injected into the reaction cell after (a). (C) Mass spectra of the water gas shift reaction on the ALE-Cu-4 catalyst: (a) injecting 5 μl of H_2O onto 50 mg of reduced ALE-Cu-4 catalyst at 298 K in a helium stream of 100 ml min^{-1}; (b) and (c) CO stream of 100 ml min^{-1} passed over the ALE-Cu-4 catalyst at 298 K after (a).

Fig. 2A shows the IR spectra of CO adsorbed on the reduced ALE-Cu-4 catalyst as a function of temperature. No detectable IR spectrum of CO adsorbed on a pure SiO_2 support was observed at 298 K. The IR band belonged to linear CO adsorption on the Cu surface in Fig. 2A, which had two principal peaks, positioned at 2122 cm^{-1} (the L_1 state) and 2133 cm^{-1} (the L_2 state). The IR intensity of CO adsorption gradually declined as the temperature increased; however, a small amount of L_2-CO still remained on the Cu surface, even at 773 K. Fig. 2B shows the IR spectra of co-adsorption of CO and H_2O on the ALE-Cu-4 sample at room temperature. First, CO adsorption was carried out in a pure 30 ml min^{-1} CO stream at atmospheric pressure for 30 min, then by passing a 30 ml min^{-1} helium stream for 30 min to purge the CO gas from the system (spectrum (a) in Fig. 2B). Surprisingly, CO adsorbed on the Cu surface almost disappeared and led to CO_2 formation within 3 min at room temperature when 5 μl of H_2O was injected into the reaction cell, as shown in spectrum (b) in Fig. 2B. However, there have been no reports in the literature that copper-based catalysts could provide high activity for the WGS reaction at room temperature, as observed in the ALE-Cu/SiO_2 catalyst used in this study. Fig. 2C shows the results of quadrupole mass spectrometer-monitored H_2O decomposition and the WGS reactions on ALE-Cu-4 catalyst at room temperature. Spectrum (a) in Fig. 2C is the time profile of the mass spectrum of hydrogen from injecting 5 μl H_2O onto 50 mg of reduced ALE-Cu-4 catalyst at 298 K under a helium stream of 100 ml min^{-1}. One can see that H_2O could be rapidly dissociated to produce H_2 at room temperature. After a dosing amount of 5 μl of H_2O, a feed CO stream of 100 ml min^{-1} was passed through the H_2O pre-covered ALE-Cu-4 sample at 298 K, leading to mass signals for H_2 and CO_2 detected by QMS, as shown in spectra (b) and (c).

Table 1 Properties of reduced IM-Pt/SiO_2, IM-Cu/SiO_2 and ALE-Cu/SiO_2

Catalysts	Temperature/K	Dispersion (%)	Particle size/nm	Surface area/m^2 g^{-1}	Surface atoms/10^{19} g^{-1}	CO adsorption/10^{19} g^{-1}
5.6% IM-Pt/SiO_2	—	24[a]	4.7[a]	3.6[a]	4.2	3.3
10.3% IM-Cu/SiO_2	—	8[b]	17.6[b]	7.3[b]	10.7	0.05
2.4% ALE-Cu-1	433	42[b]	3.30 ± 0.21	6.5[b]	9.6	0.75
2.8% ALE-Cu-2	443	36[b]	3.40 ± 0.25	8.0[b]	11.7	0.60
2.6% ALE-Cu-3	453	43[b]	3.21 ± 0.26	7.2[b]	10.6	0.84
2.5% ALE-Cu-4	463	40[b]	2.90 ± 0.29	6.5[b]	9.5	0.74

[a] Determined by H_2 chemisorption. [b] Determined by using TPR of Cu oxidized by N_2O.

Table 2 Comparison of the catalytic activity of pulse WGS and H_2O dissociation reactions on IM-Pt/SiO_2, IM-Cu/SiO_2 and ALE-Cu/SiO_2 catalysts, performed by injecting 5 μl H_2O onto 50 mg catalysts in a pure CO stream and a He stream, respectively

	TOF of H_2 from WGS and H_2O dissociation reactions/s^{-1}			
Catalysts	298 K	373 K	473 K	573 K
IM-Pt/SiO_2	0.10[a](0.70)[b]	0.16(0.77)	0.32(0.76)	5.16(0.75)
IM-Cu/SiO_2	0.01(0.01)	0.01(0.01)	0.03(0.01)	0.39(0.01)
ALE-Cu-1	0.35(0.52)	0.31(0.60)	0.51(0.61)	7.0 (0.62)
ALE-Cu-2	0.28(0.32)	0.30(0.37)	0.45(0.37)	5.67(0.38)
ALE-Cu-3	0.13(0.31)	0.19(0.38)	0.37(0.41)	5.48(0.42)
ALE-Cu-4	0.10(0.38)	0.18(0.41)	0.54(0.45)	6.01(0.47)

[a] Turnover frequency of H_2 production from the water gas shift reaction. [b] Turnover frequency of H_2 production from water dissociation.

Table 2 compares the turnover frequency of pulse WGS and H_2O dissociation reactions on all ALE-Cu/SiO_2, IM-Pt/SiO_2 and IM-Cu/SiO_2 catalysts. All catalysts were created by injecting 5 μl of H_2O onto 50 mg of catalyst in a pure CO stream and a He stream, respectively. The ALE-Cu/SiO_2 catalysts, revealing an effect of the Cu nanoparticles, showed dramatically high activity for the water gas shift and water dissociation reactions in comparison with IM-Cu/SiO_2. The Pt/SiO_2 sample allowed a larger amount of CO to be adsorbed and had a slightly higher turnover frequency (TOF) for H_2O dissociation than ALE-Cu/SiO_2, but the catalytic property of the ALE-Cu/SiO_2 catalysts also provided a higher level of TOF than the IM-Pt/SiO_2 catalyst at 298–573 K, for the WGS reaction. These observations are probably associated with intermediate formation from adsorbed CO interacting with H_2O-related species in WGS reaction. Hydrogen generation from the WGS reaction on Cu surfaces may involve complicated mechanisms, such as redox and formate pathways, but it remains controversial.[10] Shido and Iwasawa[11] also indicate that formate species can further react with H_2O to produce H_2 and generate unidentate carbonate for CO_2 formation. Regardless, water dissociation should be the essential part of the WGS reaction. Comparing larger particles of Cu, one still can see that Cu nanoparticles effectively improved the catalytic activity for the WGS reaction, because of enhancement of CO adsorption and H_2O dissociation.

The assignments of the IR bands of CO adsorbed on the reduced Cu surface have been suggested.[12,13] The IR bands below 2100 cm^{-1} were assigned to CO adsorbed on low index planes, such as the (111) and (100) faces.[12–14] The band at 2102–2118 cm^{-1} was from CO adsorbed on imperfect sites, such as step and edge sites. The CO bands above 2120 cm^{-1} might be from CO adsorbed on highly dispersed supported copper particles.[12,15,16] In this paper, the IR spectra of CO adsorbed on the ALE-Cu/SiO_2 catalysts tended toward higher stretching frequencies at 2122 and 2133 cm^{-1}, an effect which might be derived from the effect of nanoscale copper particles.

In general, traditional wet chemistry methods can produce Cu particles as small as several nanometres, but they suffer from an uncontrollable size distribution. The results of Table 1 and Fig. 1 have shown that the ALE method can produce narrow size distributions ($<10\%$ root mean square diameter) of nanoscale copper particles on SiO_2. The nanoparticles of copper apparently behaved very differently from their bulk forms, possibly because of the electronic and structural effects of the materials. The copper was supported by the porous substrate, SiO_2, and copper nanoparticles might thus have been buried inside the substrate. Some authors have indicated that the small Cu particles or isolated Cu atoms on oxide supports could be partially electropositive as a result of interaction with oxygen atoms at the surface of the support, even if the copper is reduced.[13,14]

Wang *et al.* have shown that the reaction barrier for water dissociation on an oxygen-covered copper surface was lower than that on a clean copper surface.[17] It has been reported that the formation of the H_2O–OH complex was the driving force for lowering the barrier for water dissociation on copper surfaces.[18] For water dissociation on oxygen-preadsorbed metal surfaces, adsorbed oxygen abstracts hydrogen from water to produce hydroxyls ($H_2O + O \rightarrow 2OH$).[17] Our results show that copper nanoparticles produced *via* the ALE method might lead to a partially positive charge on the copper surface. This phenomenon was deduced to be the essential factor for inducing and enhancing water dissociation, leading to high reactivity for the WGS reaction.

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