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Properties of $Cu(thd)_2$ as a Precursor to Prepare Cu/SiO_2 Catalyst Using the Atomic Layer Epitaxy Technique

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The atomic layer epitaxy (ALE) technique, originally introduced in the early 1970s by Suntola, has been widely used to deposit thin films of solid materials in semiconductor applications.[1−3] Recently, the ALE technique has also been applied to prepare some supported catalysts such as Co, Pd, Cr, and Ni in hydrogenation and dehydrogenation reactions.[4−10] It has been reported that the ALE catalysts have high metal dispersion and reactivity. However, the copper catalysts prepared by ALE technique usually attract less attention. Copper-based catalysts are frequently used in a variety of industrial hydrogenation processes, including methanol synthesis or low-temperature water-gas-shift reaction.[11−16] Two major factors restricting further use of copper-based catalysts are poor thermal stability and low metal dispersion. The ALE technique is a surface-controlled layer-by-layer process that deposits thin films in an atomic scale through self-limiting surface reactions.[17] Such a method is also expected to produce nanoscale metal catalysts. In this communication, we have used the ALE technique to prepare the Cu/SiO_2 catalyst, which may have high dispersion and small particles. The newly developed ALE-Cu/SiO_2 catalyst was expected to exhibit catalytic behavior different from that of the typical Cu-based catalysts and to provide efficient catalytic activity for CO_2 hydrogenation.

The ALE-Cu/SiO_2 was 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 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. The adsorption temperature of $Cu(thd)_2$ on SiO_2 support was 433 K. The reaction time for $Cu(thd)_2$ on the SiO_2 support was 8 h. All Cu/SiO_2, Pt/SiO_2, and Pd/SiO_2 samples used in this study were prepared by impregnating the SiO_2 from Aldrich Ltd. with an aqueous solution of $Cu(NO_3)_2$, H_2PtCl_6, and 0.05 M $PdCl_2/HCl$, respectively. All catalysts were calcined in air and reduced in pure H_2 at 573 K for 5 h before use. Carbon dioxide hydrogenation was carried out over a fixed-bed reactor at atmospheric pressure. Samples of catalysts (0.05 g) were used for the reverse water-gas-shift (RWGS) reaction. The specific Cu^0 surface areas and dispersion of the Cu catalysts were determined by the well-known N_2O chemisorption and TPR methods.[18] All Cu^0 on the catalyst was carefully oxidized by a N_2O stream and is represented by the reaction: $2Cu_{(s)} + N_2O \rightarrow Cu_2O_{(s)} + N_2$. The monolayer Cu_2O on the catalyst surface after N_2O chemisorption was reduced through a TPR process. The Cu^0 surface area is calculated by assuming a molar stoichiometry of $N_2O/Cu = 0.5$. The average value of the surface density of Cu metal is 1.46×10^{19} copper atoms/m^2. The average particle size of Cu was calculated from the Cu surface area by the formula: $d = 6V/A$.[19] TPD spectra were collected with a quadruple mass spectrometer (VG Smart IQ$^+$). The heating rate of TPD was 10 K min^{-1}. These desorbed products were admitted into the vacuum chamber with He 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.

Table 1 lists the comparison in dispersion, Cu surface area, Cu particle size, and XPS results for all Cu catalysts. The catalysts used in this study were the following: the ALE-Cu/SiO_2, IM-Cu/SiO_2, and commercial $Cu/ZnO/Al_2O_3$ (Süd-Chemie Catalysts, Inc.) catalysts. About 42% dispersion was obtained with the 2.4% ALE-Cu/SiO_2 catalyst. The dramatic dispersion of ALE-Cu catalyst was markedly larger than that of the 10.3% Cu/SiO_2 catalyst preparation, resulting from the typical impregnation method. The $Cu/ZnO/Al_2O_3$ catalyst gave the highest Cu surface area because of its higher copper content. The 10.3% IM-Cu/SiO_2 catalyst showed a slightly higher Cu surface area than ALE-Cu/SiO_2. The ALE-Cu/SiO_2 catalyst exhibited the smallest particle compared to other Cu catalysts. As all reduced Cu catalysts were treated in a helium stream at 773 K for 56 h, it is interesting to note that the Cu surface areas of IM-Cu/SiO_2 and $Cu/ZnO/Al_2O_3$ catalysts significantly decreased due to Cu sintering, and the ALE-Cu/SiO_2 retained high thermal stability of copper. The IM-Cu/SiO_2 and $Cu/ZnO/Al_2O_3$ catalysts had 53 and 82% loss of copper surface area, respectively, but the ALE-Cu/SiO_2 merely had a 12% reduction in copper surface area. However, copper, a so-called low-temperature catalyst, was usually used below 573 K due to its poor thermal stability. Thus far there have been no reports in the literature that copper/oxide catalysts could provide such thermal stability under such a high temperature as did the ALE-Cu/SiO_2 catalyst used in this study. The Cu $2P_{2/3}$ XPS spectrum of ALE-Cu/SiO_2 shows slightly higher binding energy than that of IM-Cu/SiO_2, which may imply lower electron density appearing on the ALE-Cu/SiO_2 surface.

The RWGS reaction was applied to examine the catalytic activity on these Cu catalysts and on some precious metal catalysts. The dependence of a specific TOF on time on stream for comparison of the $CO_2 \rightarrow CO$ reaction over the ALE-Cu/SiO_2, IM-Cu/SiO_2, and $Cu/ZnO/Al_2O_3$ catalysts is shown in Figure 1A. The ALE-Cu/SiO_2 containing low copper concentration presented the highest TOF value. The 10.3% IM-Cu/SiO_2 gave a copper surface area similar to that of 2.4% ALE-Cu/SiO_2, but exhibited weak catalytic activity for CO_2 hydrogenation. The ALE-Cu/SiO_2 provided higher TOF than the IM-Cu/SiO_2 within 12 h by a factor of about 14−24. In Figure 1B, the CO_2 conversions over the 2.4% ALE-Cu/SiO_2, 2%

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Table 1. Comparison of the $Cu/ZnO/Al_2O_3$, IM-Cu/SiO_2, and ALE-Cu/SiO_2 Catalysts

catalysts	Cu content wt %	dispersion (%)	particle size (nm)	Cu surface area[a] (m^2/g)	Cu surface area[b] (m^2/g)	XPS of Cu $2P_{2/3}$ (eV)
$Cu/ZnO/Al_2O_3$	20	15	6.5	23	4.2	−
IM−Cu/SiO_2	10.3	8	17.6	7.3	3.4	932.3
ALE-Cu/SiO_2	2.4	42	2.4	6.7	5.5	932.8

[a] All Cu catalysts were calcined in air and reduced in pure H_2 at 573 K for 5 h. [b] All reduced Cu catalysts were treated in helium stream with 50 mL min^{-1} at 773 K for 56 h.

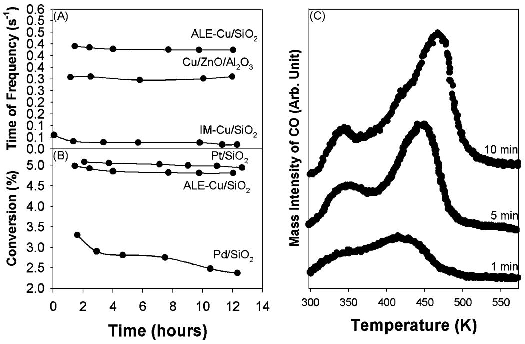

Figure 1. (A and B) The dependence of CO_2 conversion on reaction time for H_2/CO_2 with 1:1 ratio and 100 mL min^{-1} over catalysts at 773 K. (C) TPD spectra of CO from 2.4% ALE-Cu/SiO_2 with various dosing amounts of CO. The adsorption of CO was carried out in a CO stream with 30 mL/min flow rate.

Pt/SiO_2, and 2% Pd/SiO_2 catalysts are also compared as a function of time. The ALE-Cu/SiO_2 and Pt/SiO_2 retained stable catalytic activity within 12 h. The Pd/SiO_2 catalyst provided a lower reaction rate, whereas the CO_2 conversion decreased with time. In general, the activity of precious metal catalysts will provide higher activity in WGS and RWGS reactions than Cu-based catalysts,[20−22] but the activity of ALE-Cu/SiO_2 is comparable to those of Pt and Pd catalysts in the present study.

Figure 1C shows the TPD spectra of CO as a function of CO exposure on reduced ALE-Cu/SiO_2 catalyst. Copper has a completely filled 3d band ($4s^13d^{10}$) and no d-states at the Fermi level; therefore, CO generally desorbed from the Cu surface below room temperature because CO weakly bonded with the Cu surface. In this present study, no detectable TPD spectra of CO were observed from the IM-Cu/SiO_2 surface when large amounts of CO were exposed at room temperature. Nevertheless, it was surprising to see that CO molecules strongly bonded to the ALE-Cu/SiO_2 surface and had two desorption peaks observed at approximately 343−353 and 443−463 K. The catalytic property of the ALE-Cu/SiO_2 catalyst was obviously different from the typical impregnating Cu/SiO_2 catalyst. The ALE method produced the smaller Cu particles and might have partially filled the 3d band with high density of states at the Fermi level. The ALE-Cu/SiO_2 was characterized by transmission electron microscopy (TEM, PHILIPS CM-200, 200 kV) as shown in Figure 2. In accordance with the measurement of particle size in Table 1, a large amount of small nanoscale Cu particles of the ALE-Cu/SiO_2 was observed in the TEM image.

In summary, we have shown that the ALE method coduld make high-dispersion and nanoscale Cu/SiO_2 catalysts. The ALE-Cu/SiO_2 has a very different characterization in comparison with typical Cu-based catalysts. It was found that the ALE-Cu/SiO_2 catalyst had satisfactory thermal stability to resist the sintering of Cu particles under high-temperature condition. Due to the small Cu particle formation, the ALE-Cu/SiO_2 could strongly bind CO and provide highly catalytic activity for CO_2 converted to CO.

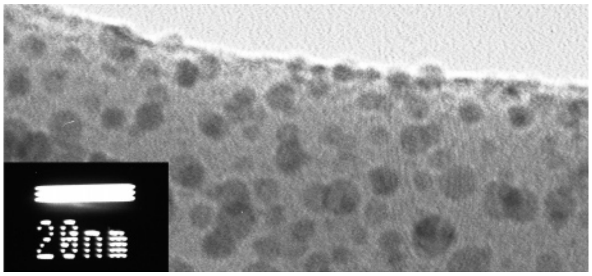

Figure 2. TEM image of ALE-Cu/SiO_2 after calcinations and reduction.

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