Chemical Vapor Deposition of Gold Nanoparticles on MCM-41 and Their Catalytic Activities for the Low-temperature Oxidation of CO and of H_2

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Au nanoparticles can be deposited on MCM-41 by chemical vapor deposition (CVD) of dimethyl gold acetylacetonate. They exhibit high catalytic activities for the oxidation of CO and of H_2 at low temperatures, below and above 273K, respectively.

Ordered mesoporous molecular sieves like MCM-41 and MCM-48[1,2] have motivated us to explore new and exciting opportunities for catalytic, sorption, and separation applications[3]. In addition to the syntheses of metal-substituted mesoporous molecular sieves[2], attempts to incorporate metals[4,5] and metal oxides[6] into mesoporous channels with an uniform width have recently been made expecting unique size effects on the physical and chemical properties of the materials. In order to prove channel connectivity by using a high resolution transmission electron microscopy, wire-shaped platinum was incorporated into the channels of a few mesoporous molecular sieves[4,5] by a cation exchange method. A variety of semiconductive metal oxides were also incorporated into the channel to examine the quantum size effect on the band gap energies[6]. The catalytic properties of metalloporphyrins[7] and of Pt particles[8,9,10] which were incorporated into the mesopores of FSM-16 were studied.

In this work, chemical vapor deposition (CVD) method[11] is used for depositing Au on MCM-41. Although platinum was deposited on MCM-41 as nanoparticles by an ion exchange method,[4,5] Au could not be deposited on SiO_2 by the same method probably because the melting point of Au (1336K) is much lower than that of platinum (2042K). Highly dispersed Au particles are usually prepared by liquid phase methods, for example, coprecipitation[12] and deposition-precipitation,[13] where the point of zero charge (P.Z.C.)[14] of the support is a dominant factor for their availability. Because the pH of $HAuCl_4$ solution should be adjusted in the range of 6 to 10 to deposit $Au(OH)_3$ on the surface of support metal oxide[15], metal oxides with P.Z.C. far below pH=6 are negatively charged and do not allow $Au(OH)_3$ to deposit on their surfaces. Silica (P.Z.C. : about 2) is such a typical example.

As a gold precursor for CVD method, $(CH_3)_2Au(CH_3COCHCOCH_3)$, abbreviated to $Me_2Au(acac)$, was used without further purification of the reagent available from Tri Chemical Laboratory Inc.. Its vapor pressure at room temperature was about 8.5×10^{-3} torr. The MCM-41 supports were prepared by a method reported in the literatures.[1,2] They have mesopore widths of 22, 27, 31Å with specific surface areas of 1010, 1036, and 979m^2/g, respectively. For comparison with liquid phase methods, $Au(H_2NCH_2CH_2NH_2)Cl_3$ was used as a cationic gold precursor to impregnate into MCM-41 with Au loadings as high as those by CVD. Silica support used for comparison with MCM-41 in catalytic activity was silica gel, type G of Fujisilycia Chemical co. Ltd., with a specific surface area of 310 m^2/g.

The CVD experimental setup was made of hard glass. The lowest pressure that could be reached in this line was about 10^{-3} torr. MCM-41 and SiO_2 gel were evacuated at 473K for 4 hours to remove adsorbed water and were then treated with 20 torr oxygen gas at 473K for 30 min. to remove organic residue and to oxidize the surface. The precursor vessel was heated to a fixed temperature of 306K to gradually evaporate a measured amount of $Me_2Au(acac)$. The precursor adsorbed on the metal oxide supports which were mounted in the reaction vessel was then calcined in air at 473K~773K to decompose into metallic Au particles on the support surface.

Figure 1 shows a TEM photograph for Au deposited on MCM-41 (22Å) by CVD. Both dark rod-like images and spherical images are seen. The shorter width of rod-like particle was taken as the diameter of rod-like particles. The mean diameter of all particles is 4.2 nm and that of rod-like particles is 3.4 nm. The mean diameter and the most frequent diameter of rod-like Au particles in Figure 2 are almost equivalent to the width of the d_{100} value (33.9Å) which includes mesopore width and thickness of MCM-41 wall. Therefore, the apparent growth of Au rods or wires along with the channels of the support strongly suggests that many Au particles are incorporated into the

Table 1. Mean diameters of gold particles and kinetic parameters of CO and H_2 oxidation for Au supported on MCM-41 and on SiO_2

Catalyst[1)]	method	Au[2)]	D_{Au}	CO oxidation $T_{1/2}$	E_0	TOF[5)]	H_2 oxidation $T_{1/2}$
		wt%	nm	K	kJ/mol	s^{-1}	K
Au/MCM-41(22Å)	CVD	4.2	4.2±1.4[3)]	263	26	0.02	303
Au/MCM-41(27Å)	CVD	2.9	4.0±1.5[3)]	259	27	0.05	302
Au/MCM-41(31Å)	CVD	3.5	4.9±1.9[3)]	264	23	0.04	310
Au/SiO_2[6)]	CVD	6.6	6.6±3.8[3)]	227	17	0.02	329
Au/SiO_2	IMP	14.7	20.0[4)]	477	-	-	357
Au/MCM-41(22Å)	IMP	6.8	16.1[4)]	608	-	-	380
Au/TiO_2[6)]	CVD	4.7	3.8±2.7[3)]	239	41	0.02	321

1)Calcined in air at 673K for 4hrs . 2)ICP analysis. 3)TEM, 4)XRD, 5) Turnover frequency at 273K, 6) ref.16.

channels of the MCM-41 support. It is also seen that spherical and hemispherical Au particles are mostly deposited on the disordered parts of MCM-41. The mean diameters of Au particles deposited by CVD on MCM-41 with mesopore widths of 27 and 31Å are 4.0 and 4.9 nm, respectively, and are much smaller than that of Au/SiO_2. This result shows that the fine ordered channel structure keeps the Au particles small.

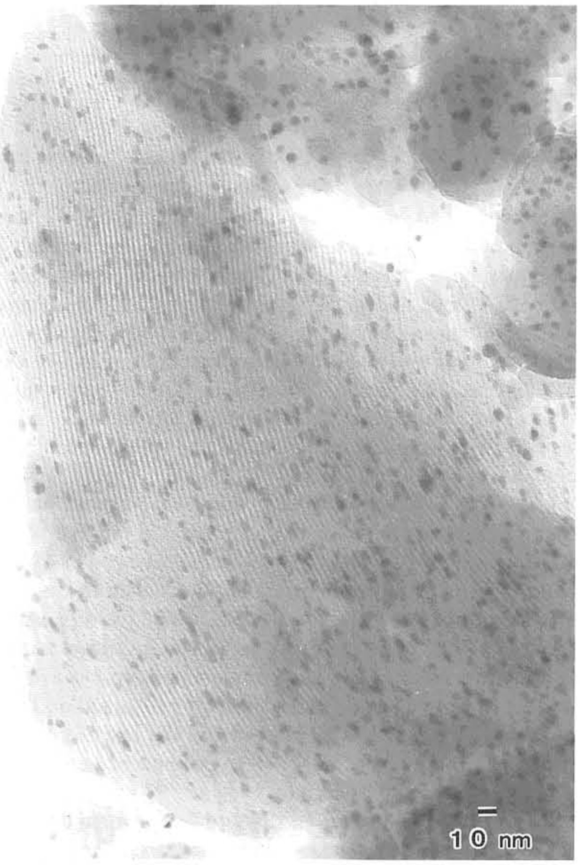

Figure 1. TEM photographs of 4.2wt.% Au/MCM-41 prepared by CVD and calcined in air at 673K for 4 hours.

The catalytic activities of Au/MCM-41 were examined for the oxidation of CO and of H_2 (SV=20,000 ml/h g-cat., reactant gas : 1 vol% H_2 or CO in air, fix-bed flow reactor). The results were summarized in Table 1. Au/MCM-41 samples prepared by CVD and calcined in air at 673K for 4 hours exhibit high catalytic activities for H_2 oxidation. The catalytic activity of H_2 oxidation is almost independent of the type of metal oxide supports and is primarily proportional to the exposed Au surface area[9]. The fact that temperatures for 50% conversion of H_2 are below 310K and are as low as those for Au(13 wt%)/Fe_2O_3 and Au(13 wt%)/Al_2O_3 prepared by coprecipication[9] also supports TEM observations that ultrafine Au particles are highly dispersed on MCM-41. Au/MCM-41 samples exhibit higher catalytic activities in CO oxidation than in H_2 oxidation. CO oxidation took place at temperatures below 273K and the deactivation of the catalysts was not observed at 273K for 4 hours.

Because no reliable gas adsorption technique was available for the determination of the number of Au atoms exposed on the surface, we calculated them based on the mean diameters of Au particles and the actual Au loadings determined by ICP (Induced Coupled Plasuma) analysis. Therefore, the TOF values calculated can present only a rough comparison of the order of magnitudes. TOF values for CO oxidation at 273K are in the same order as those for Au deposited on SiO_2 by CVD and on TiO_2, Fe_2O_3, and Co_3O_4 by liquid phase methods.[15] It is likely that Au particles incorporated into the channel of MCM-41 do not participate in the reaction. The similar TOF values implies that Au particles incorporated deep into the mesopore channels do not constitute the majority and/or smaller Au particles, especially, these less than 30Å lead to higher TOF.[15]

On the other hand, Au/MCM-41 prepared by IMP has poor dipersion of Au with a mean particle diameter of about 20 nm. It can oxidize only half of CO even at 608K and exhibits much lower catalytic activity for CO oxidation than for H_2 oxidation, indicating weak interaction between Au particles and the support. The large differences between CVD and IMP methods in both the mean diameter of Au particles and the catalytic activities are in accordance with the results obtained for Au/SiO_2 gel.[16]

In conclusion, this communication reports that chemical vapor deposition of organogold complex on MCM-41 is an effective technique to deposit Au nanoparticles on MCM-41 and that the Au/MCM-41 catalysts thus obtained are very active for the oxidation of CO and of H_2 at temperatures below 310K and much more active than those prepared by the conventional impregnation method.

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