

In situ Synthesis of Gold Nanoparticles inside the Pores of MCM-48 in Supercritical Carbon Dioxide and its Catalytic Application

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Abstract: Gold nanoparticles are deposited into the channels of MCM-48 through a simple H₂-assisted reduction of HAuCl₄ (aqueous solution) in supercritical carbon dioxide medium at 70 °C within 2–4 h. The nanoparticles were characterized by powder X-ray diffraction (PXRD), N₂ adsorption-desorption, transmission electron microscopy (TEM), and UV-Vis spectroscopy. The particle size of the synthesized material is tunable with the pressure (density) of the supercritical carbon dioxide medium. At the fixed temperature (70 °C) and hydrogen pressure [$P(\text{H}_2) = 2$ MPa], the Au particle size varies from *ca.* 25 nm to *ca.* 2 nm with the change in CO₂ pressure from 7 MPa to 17 MPa. At the low solvent density conditions, larger particles of ~25 nm were obtained. On the contrary, a high solvent density of CO₂ slows down particle aggregation, resulting in the small particle size within the range of 2–5 nm. This change in particle size with CO₂ pressure and the interaction

of the particles with the silica support were correlated well with long-range van der Waals interactions and consequently the Hamaker constant for the gold nanoparticle-CO₂ (A_{131}) and silica-gold core-CO₂ (A_{132}), respectively. Supercritical carbon dioxide alone can provide a unique environment for stabilizing gold nanoparticles in the channels of the cubic mesoporous MCM-48 support and exquisite control of the particle size without perturbing the support structure. The synthesized material is highly stable, recyclable and no metal nanoparticle leaching was observed. The selective hydrogenation of crotonaldehyde with the synthesized material provides convincing evidence that the particles are inside the pores and available to the reactant molecules.

Keywords: gold; mesoporous materials; nanoparticles; selective hydrogenation; supercritical fluids

Introduction

In the past decades, metal nanoparticles have attracted much attention because of the unique size dependence of their optical, catalytic, semi-conductive and magnetic properties.^[1–5] These distinct properties may be attributed to the quantum confinement phenomenon derived from the change in density and effective band gap of the electronic energy level, as well as to the high ratio of surface to bulk atoms. Therefore, one of the key challenges is the synthesis of nanoparticles of specific size and shape that would provide significant opportunities in various applications. In particular, gold nanoparticles are very attractive for nanotechnology research because of their exciting optical properties and catalytic activities.^[6–8] Generally, gold nanoparticles are synthesized by the wet impregnation method,^[9] synthetic insertion,^[10] co-assembly^[11] and a surface sol-gel modification method.^[12] However, these processes have some difficulties with

the availability of the metal precursor in terms of high volatility, perturbation of the support surface structure, non-uniform distribution of the particles and particle aggregate formation. In a recent approach, a sonochemical method was used to diffuse the nanoparticle through the solvent inside the pores of the mesoporous material, which was undesirably slow due to the low diffusivity of the medium.^[14]

The potential use of supercritical carbon dioxide (scCO₂) has attracted much interest as a sustainable and “green” medium for material synthesis. It can be handled easily because it is non-toxic, non-flammable and inexpensive. The unique properties of scCO₂ combine the advantages of liquid phase and gas phase processes. The tunable density of scCO₂ can be controlled to match that of the liquid phase, which enables the medium to dissolve the metal precursor. On the other hand, low viscosity, high diffusivity and zero surface tension, which are closer to the gas phase, eliminate precursor volatility constraints and facilitate

the particle deposition within the confined geometries. The miscibility of scCO_2 with the reducing gasses like H_2 mitigates the mass transfer limitation, which is common in liquid phase reductions.

Several metal nanoparticles^[15–17] were prepared in scCO_2 . The conventional approaches for the synthesis of nanoparticles are the rapid expansion of supercritical solution (RESS) and the supercritical antisolvent (SAS) techniques. These techniques, however, face the difficulties of dispersibility due to very low van der Waals forces and the polarizability of the medium. To resolve this, Johnston and Kogel^[18] used expensive and non-biodegradable fluorinated ligands, but the problems of carrier solvent solubility and ligand by-products formation still remains. In another approach, water in a CO_2 micro-emulsion as a “nanoreactor” was used to synthesize metal nanoparticles.^[19,20] Even though the size, shape and particle morphology can be controlled, it is difficult to collect the prepared sample owing to aggregation and coalescence. With regard to catalytic activities, these metal nanoparticles often suffer from modest activity and decreased life due to aggregation. In a recent approach, pre-synthesized gold nanoparticles (size range 2.2–3.4 nm) were impregnated successfully into the channels of different mesoporous silica supports in scCO_2 -toluene medium.^[21] However, the pre-synthesized particles need isolation from the by-products, and cleaning before impregnation. Therefore, the *in situ* syntheses of nanocrystals within the channels of porous material without perturbing the support structures still remain a challenge.

In this work, we have successfully applied the H_2 -assisted reduction of an aqueous solution of HAuCl_4 to the formation of gold nanoparticles inside the pores in scCO_2 medium. The key advantages of our method are the use of an aqueous solution of HAuCl_4 , which prevented the problem of ligand adsorption, unwanted by-product formation and maintained the support structure after nanoparticle formation. Moreover, this method offers a simple and convenient synthesis process with the good control over the particle size, devoid of any harsh reducing agent, organic solvent-free synthesis and no further antisolvent or stabilizing surfactant is necessary. The catalytic activity of the synthesized material to the selective hydrogenation of crotonaldehyde with respect to the gold particle size has also been monitored to validate the nanoparticle deposition inside the channels of MCM-48.

Results and Discussion

The formation of gold nanoparticles on MCM-48 was confirmed by the change of color from white to pink. Gold nanoparticles exhibit a clear optical signature

which correlates well with the particle size and the variation of CO_2 pressure. For example, purple to rich pink colored samples are obtained at 7–10 MPa of CO_2 whereas, above 10 MPa the sample color changes from light pink to colorless (see Figure 2, panel a). The color scenario of the synthesized material was expected to give some primary idea about the size of the gold metal particles, like <2 nm for colorless particles, rose pink for 2–20 nm and purple for >20 nm particles as observed on tailor-made gold nanoparticles inside the mesoporous channel.^[11] Hence, the appearance of the synthesized materials suggested a considerable influence of CO_2 pressure on particle size.

Figure 1 panel a compares the XRD pattern of the parent MCM-48 with that of Au-MCM-48 material (17 MPa). All the materials show typical low angle (211) reflections and also the (220) reflections along with the smaller Bragg's peaks in their scattering pattern, which are the characteristics of the cubic space group *Ia3d*. The presence of the similar peaks of the parent material confirmed that the overall structure of MCM-48 was retained after gold nanoparticle formation. For the parent material, the most intense (211) XRD line appeared at $2\theta = 2.52^\circ$, whereas after the incorporation of gold nanoparticles, the main peak is shifted to the lower $2\theta = 2.06^\circ$ (17 MPa) with a decrease in the intensity as well. The reduced scattering intensities of the Bragg reflections might be caused by the introduction of scattering materials into the pores^[22,23] or by the partial collapse of the ordered cubic structure due to the presence of gold nanoparticles. However, the scattering pattern of Au-MCM-48 (Figure 1, panel a) shows a series of Bragg's peaks originating from the cubic structure of MCM-48. Therefore, the reduced peak intensity of Au-MCM-48 might be due to the presence of gold particles inside the channel, rather than the collapse of the cubic structure. In order to check the stability of the Au-MCM-48 structure in terms of the amount of the gold incorporation in scCO_2 , the gold content was increased from *ca.* 1 to *ca.* 5 wt % at the fixed pressure of CO_2 (17 MPa) and H_2 (2.0 MPa). As a result, the main XRD peaks are shifted towards the lower angle and the corresponding *d* spacing of Au-MCM-48 sample increases with increasing gold content. The Au-MCM-48 (17 MPa) retained its structure up to the gold loading of *ca.* 5 wt %. The unit cell parameters ($a_0 = d_{211}\sqrt{6}$) for the parent material and Au-MCM-48 obtained at different CO_2 pressure are shown in Table 1. It has been found that the value of a_0 changes from 8.46 nm for the parent material to 10.49 nm for Au-MCM-48 (17 MPa). This increase in unit cell parameters is attributed to the pore filling of the host material, which consequently reduces the scattering contrast between the pores and the walls.^[24,25]

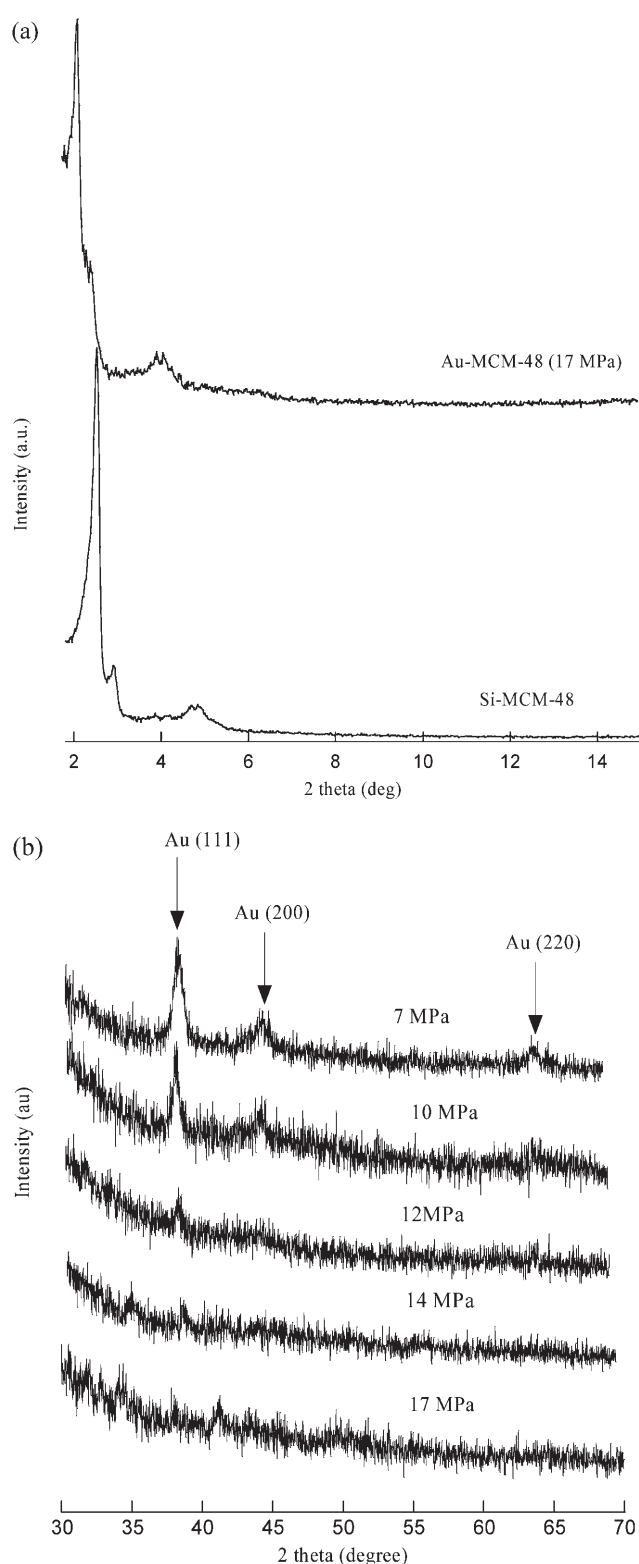


Figure 1. X-ray diffraction patterns of (a) the parent material and Au-MCM-48. (b) Wide angle XRD pattern of Au-MCM-48 at different CO₂ pressures.

To detect the gold nanoparticles, XRD measurements were carried out at the higher angle region

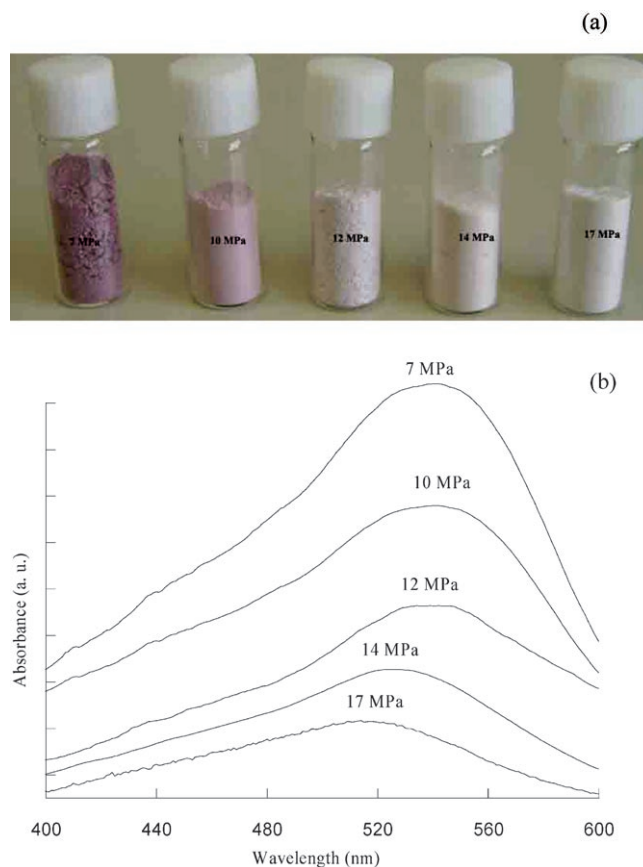


Figure 2. UV-Vis spectra of Au-MCM-48 obtained at various CO₂ pressures.

($2\theta = 30^\circ$ to 70°) and are displayed in Figure 1, panel b. Two distinctive Bragg reflections (111) and (200) of *fcc* gold are clearly observed for all the samples treated at or below 12 MPa of CO₂ at $2\theta = 38.1$ and 44.4 . However, these peaks are extremely weak for the materials obtained above 12 MPa, indicating that the nanoparticles are not within the detection limit. Using the Scherrer diffraction formula, the particle size was obtained from the FWHM of the gold (111) peak and is presented in Table 1. An increase in FWHM of the gold (111) peak corresponding to the decrease in particle size (~ 25 nm to < 2 nm) with increasing CO₂ pressure (7 MPa to 17 MPa) was observed. At the low density (low pressure) conditions, the formation of larger particles were favored, whereas smaller particles need a high density (higher pressure) to be deposited. This happens because the larger particles possess greater inter-particle van der Waals attractions and are formed at low solvation conditions (lower density), whereas the smaller particles are obtained at higher solvation conditions (higher density).^[26] Hence, the tunable solvent density of the scCO₂ medium has the unique advantage to obtain the desired size of the metal nanoparticles. This result is in the good agreement with the color

Table 1. Physical properties of Au-MCM-48, pressure-dependent gold nanoparticle-CO₂ Hamaker constant (A_{131}) and Hamaker constant (A_{132}) between silica and gold core mediated by scCO₂.

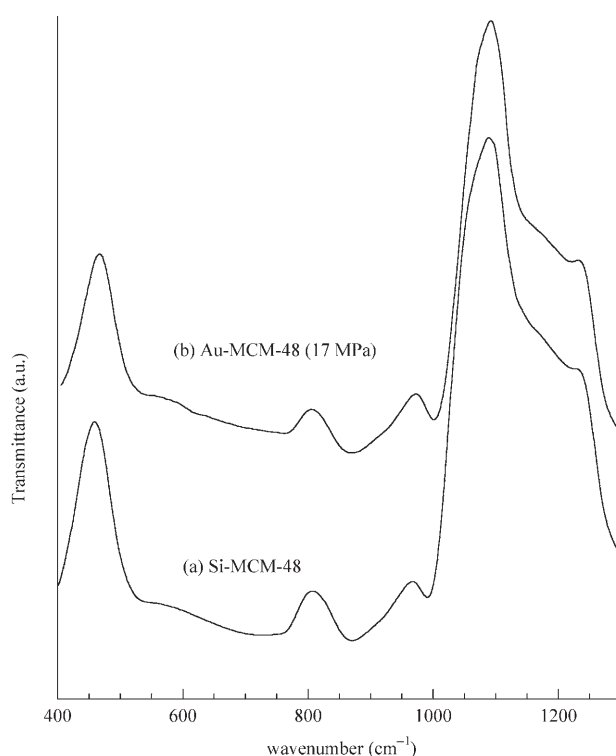
Material (CO ₂ pressure in MPa)	a_0 (nm)	Pore volume (cm ³ g ⁻¹)	BJH pore diameter (nm)	S_{BET} (m ² g ⁻¹)	Average particle diameter (nm) ^[a]	Color of the material	A_{131} (eV)	A_{132} (eV)
No gold	8.56	0.88	3.4	1050	-	white	-	-
Au-MCM-48 (7)	9.62	0.81	3.3	981	25.1	rich purple	2.345	0.858
Au-MCM-48 (10)	10.47	0.72	3.2	898	10.2	purple	2.233	0.784
Au-MCM-48 (12)	10.56	0.70	3.2	862	4.0	light Pink	2.083	0.683
Au-MCM-48 (14)	10.52	0.65	3.1	790	2.5	light pink to colorless	2.020	0.646
Au-MCM-48 (17)	10.49	0.61	3.1	760	<2	light pink to colorless	1.465	0.291

^[a] Particle size as obtained from Scherrer diffraction formula (particle size = $k\lambda/\text{FWHM} \cos\theta$, where λ is the wavelength of the Cu K $_{\alpha 1}$ line (0.154 nm), θ is the angle between the incident beam and the reflection lattice planes, and FWHM is the width (in radians) of the diffraction peak) using the line width of the gold (111) peak.

scenario of Au-MCM-48 as shown in Figure 2, panel a.

Figure 2, panel b shows the optical absorption spectra of Au-MCM-48 recorded as a function of CO₂ pressure. From the absorption spectra, we observed a monotonic increase in intensity of the surface plasmon resonance with the decrease in CO₂ pressure. According to the Mie theory,^[27] the absorption band is due to the excitation of the surface plasmon vibration. This gives the particles their characteristics pink/purple color depending on the particle size. The absorbance peaks of all the materials that were obtained below 10 MPa with large size of the nanoparticles,^[28] exhibit distinct absorption spectra in the visible region of the electromagnetic spectrum (*ca.* 545 nm), responsible for the striking purple color (Figure 2, panel b). However, a blue shift in the corresponding peak position (*ca.* 510 nm) was observed on change of CO₂ pressure to >10 MPa. The shifting of the surface plasmon resonance is due to the decrease in particle size; and these small metallic particles are attributed to quantum size effects, which leads to the formation of quantized energy states. The blue shift in the surface plasmon vibration with increasing CO₂ pressure was strongly supported by the color of the obtained material.

Figure 3, traces a and b show the spectra of the parent MCM-48 material and Au-MCM-48 (17 MPa) in the region 1300–400 cm⁻¹, respectively. The parent material shows the vibrational band at ~1090 cm⁻¹ that is assigned as the anti-symmetric stretching (Si–O–Si) vibration, while the peak at 810 cm⁻¹ is attributed to symmetrical stretching vibration of Si–O–Si. The IR spectrum remains nearly unchanged after the incorporation of gold nanoparticles. Although the wavenumber of (Si–O–Si) band decreases from 1090 cm⁻¹ (in the purely siliceous sample) to 1087 cm⁻¹ [Au-MCM-48 (17 MPa)], this shift is within the spectral resolution. It indicates that the structure of the support is maintained after the incor-

**Figure 3.** FT-IR spectra of (a) the parent material and (b) Au-MCM-48 (17 MPa)

poration of gold nanoparticles and confirmed the XRD observation. However, the displacement of the lattice vibrational bands can be observed in the wavenumber of the (Si–O–Si) band which decreases from 810 cm⁻¹ (purely siliceous MCM-48) to 795 cm⁻¹ for Au-MCM-48 (17 MPa).

Figure 4 shows the TEM images of Au-MCM-48 and the corresponding particle size distribution at different CO₂ pressures of 7 MPa to 12 MPa. The influence of CO₂ pressure as observed in the XRD (Figure 1, b) becomes obvious from the inspection of the TEM images. The number of the larger particles

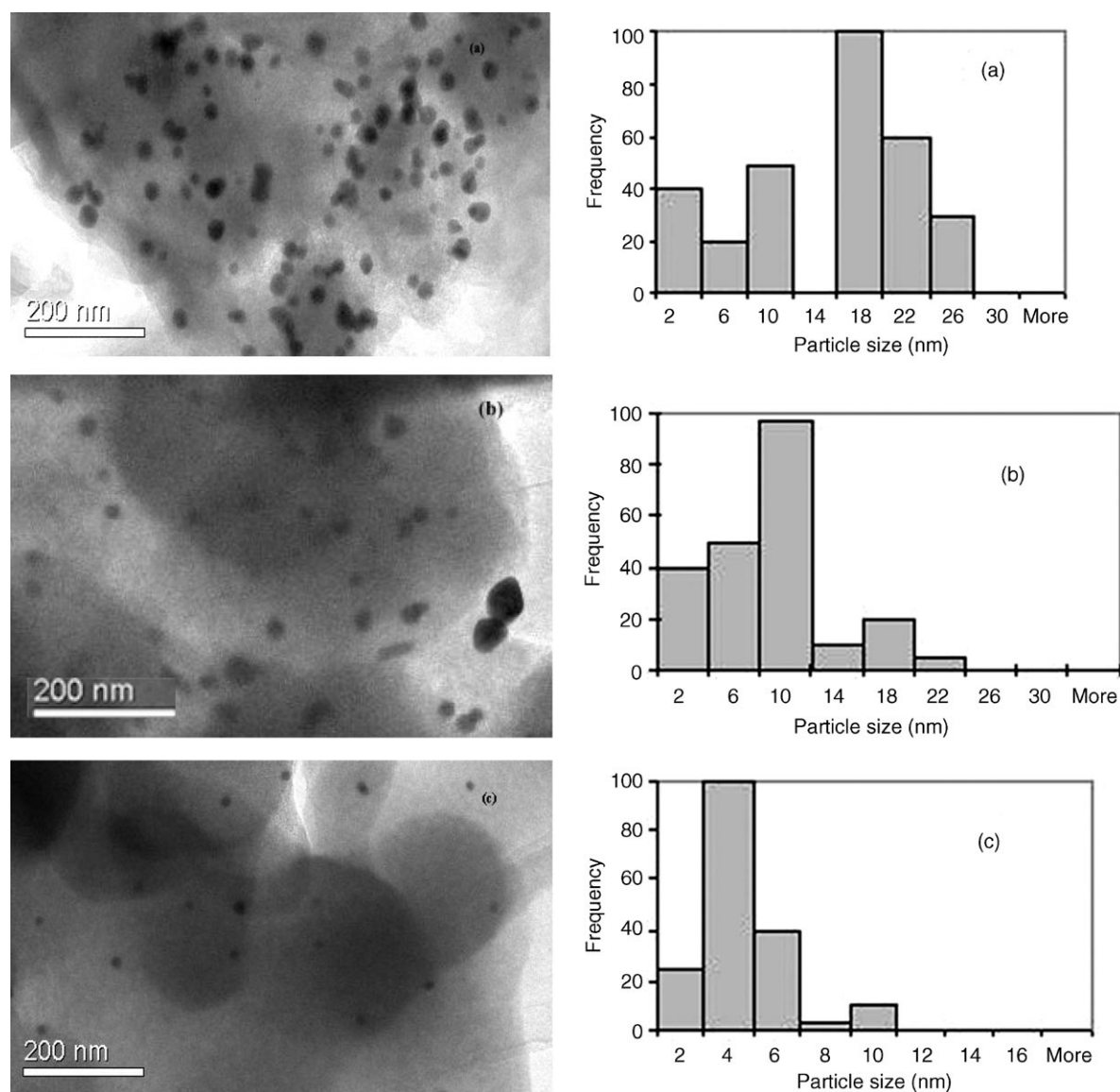


Figure 4. TEM images of Au-MCM-48 obtained at (a) 7 MPa, (b) 10 MPa, and (c) 12 MPa.

dispersed on the outer surface was more at the lower pressure of CO₂ (7 MPa; Figure 4, a), while the number decreases at the higher pressure of CO₂ (12 MPa; Figure 4, b). No larger particles are found at 17 MPa (Figure 4, c), which proves that the smaller gold nanoparticles are totally confined within the pores of MCM-48. Apparently a five-fold increase in CO₂ density leads to a decrease of 88% in the particle size. The average inter-particle distance appears to decrease with increasing particle size, possibly due to the stronger attractive van der Waals forces between the larger particles and having a less homogenous size distribution compared to the smaller one. Above 12 MPa of CO₂ pressure, where the particle size is close to the pore diameter, an increase in the number of particles inside the pores can be expected. Although the chances of pore blockage were there, high

diffusivity of the scCO₂ tends to diffuse the particles towards the center of the pore.^[29] In addition to that when particles are included inside the pores, mesoporous materials have a strong tendency to form regular pores by expansion,^[11] which was confirmed by the increase in center-center spacing (a_0 , Table 1) of the pores. It is very difficult to show any evidence by TEM for the presence of the very small (< 2 nm) gold nanoparticles produced at *ca.* 17 MPa inside the pores/channels.

The N₂ adsorption-desorption isotherms along with the pore size distribution of the parent material, Au-MCM-48 (7 MPa) and Au-MCM-48 (17 MPa) are presented in Figure 5, panels a, b and c, respectively. The isotherm of the parent material indicates a linear increase in the amount of adsorbed N₂ at low relative pressure ($P/P_0 = 0.3\text{--}0.4$) associated with capillary con-

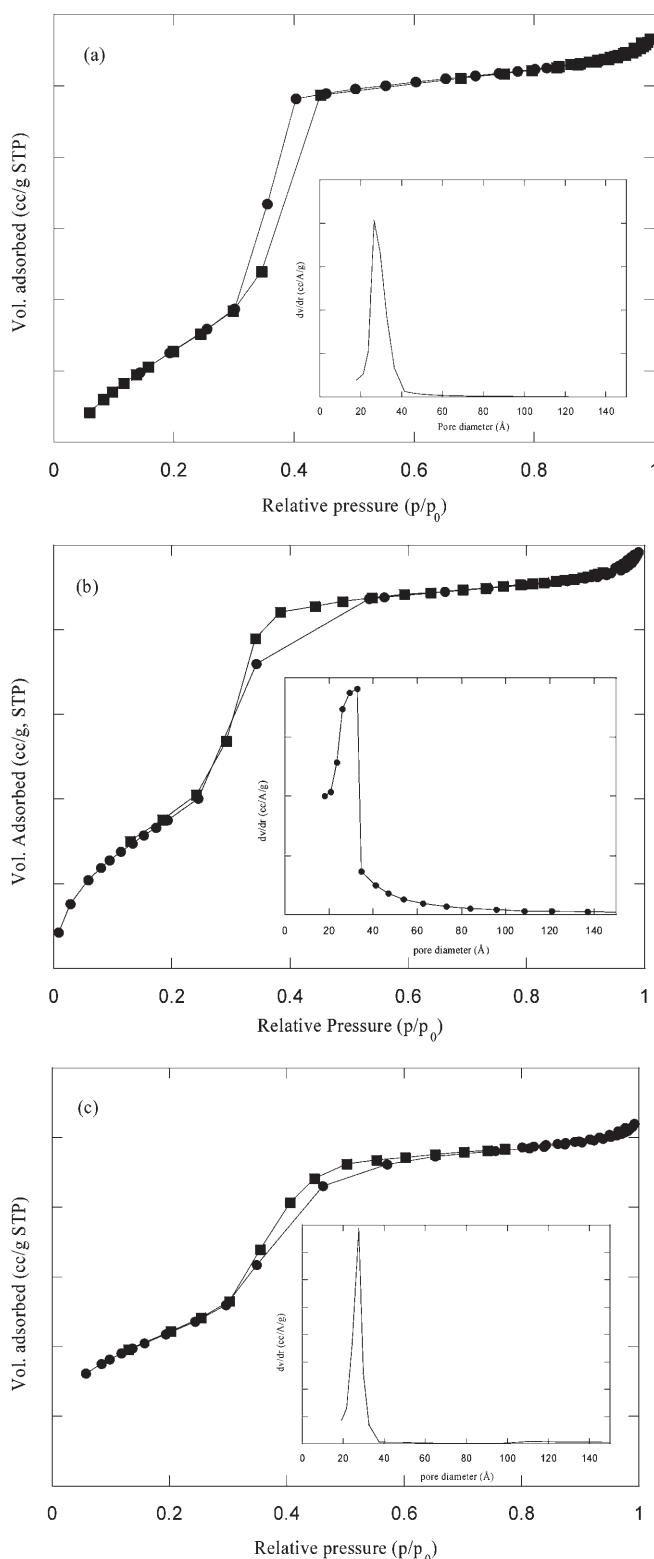


Figure 5. N_2 adsorption-desorption isotherm of (a) parent Si-MCM-48 and (b) Au-MCM-48 (7 MPa) and (c) 17 MPa.

condensation in the channels of the MCM-48 structure. According to IUPAC nomenclature the resulting isotherm can be classified as Type IV with hysteresis.

The position of the inflection point depends on the diameter of the mesopores, and the sharpness indicates the narrow pore size distribution. The height and sharpness of the N_2 condensation provides clear evidence of the high quality of the parent material with a pore diameter of 3.4 nm, a surface area of $1050 \text{ m}^2/\text{g}$ and a pore volume of $0.88 \text{ cm}^3/\text{g}$ (Table 1) which corresponds well to the literature data.^[30] The N_2 adsorption-desorption isotherm of Au-MCM-48 also shows a similar type IV adsorption isotherm (Figure 5, panels b and c). In support of the XRD data, a narrow pore size distribution was evident for all of the samples, indicating that the highly ordered structures are maintained after incorporation of the gold. No micropores were observed in the isotherm. The BET surface area, BJH pore diameter of the parent material and Au-MCM-48 obtained at different CO_2 pressure are summarized in Table 1. Compared to the parent material, there was no systematic decrease in the pore volume and the pore diameter for the samples obtained at or above 12 MPa. A slight decrease of pore volume ($0.61 \text{ cm}^3/\text{g}$) was observed for Au-MCM-48 (17 MPa). This suggests that the pores of the mesoporous channels are still accessible and could be fruitful for catalytic reaction to allow a guest molecule to diffuse into the silica in order to reach the active nanoparticles.

Supercritical CO_2 deposition is a new approach for metallization. An attempt was made to visualize the bulk phase behavior of scCO_2 at different pressures (fixed pressure of $\text{H}_2=2 \text{ MPa}$) in the presence of an aqueous solution of gold using a high-pressure view cell. A significant phase transition was observed. At the higher pressure of 17 MPa a continuous phase was formed, which indicates the formation of highly dispersed smaller particles. On the other hand, at the lower pressure of 7 MPa, two phases were clearly visible, which might be due to the possible formation of the larger particles. Although CO_2 is considered as a non-polar solvent, there is always some finite solubility of CO_2 in water depending on temperature and pressure. Moreover, from the MD simulation, Sato et al.^[31] identified a hydrogen bond between oxygen in CO_2 and hydrogen in H_2O to explain the dissolution of CO_2 in H_2O . The mechanism behind the nanoparticle formation probably consists of three steps. First, the gold aqueous solution is reduced by hydrogen, and then in the next step the reduced gold aqueous solution reacts further. In this step, the metal solution and CO_2 adsorb on the surface of MCM-48, followed by diffusion into the pores because of the higher density of CO_2 inside the pores compared to the bulk phase.^[29] Finally, CO_2 at that high density interacts favorably with the metal, and water desorbs from the surface easily and diffuses into scCO_2 , leaving the pure metal in the channels of the support.

We have experimentally observed that the adjustment of the solvent properties of scCO₂ can induce a change in the particle size, which will be explained by the interaction of the solvent with the metal particles. A theoretical approach of a soft sphere model was proposed by Shah et al.^[32] to determine the total interaction energy. The total interaction energy is obtained by the summation of attractive and repulsive forces [Eq. (1)]:

$$\Phi_{total} = \Phi_{vdw} + \Phi_{osm} + \Phi_{elas} \quad (1)$$

The attractive energy is the van der Waals attractive force resulting from the dipole-induced dipole interaction and its magnitude is reduced at larger distances. The repulsive forces are composed of the osmotic term Φ_{osm} and the elastic term Φ_{elas} . When particles are small, typically in the range of micrometers or less, and are dispersed in a solvent, van der Waals attraction forces and Brownian motion play important roles. The combination with Brownian motion would further result in the agglomeration of the nanoparticles. The attractive forces (that arise when dipoles interact across an intervening medium) between two nanoparticles are related to the particle radius R , center to center separation distance d and the Hamaker constant A by the following equation [Eq. (2)]:

$$\Phi_{vdw} = -\frac{A_{131}}{6} \left[\frac{2R^2}{d^2 - 4R^2} + \frac{2R^2}{d^2} + \ln \left(\frac{d^2 - 4R^2}{d^2} \right) \right] \quad (2)$$

where the negative sign represents the attraction nature of the interaction between two particles. The Hamaker constant A_{131} is a proportionality factor that accounts for the interaction between two nanoparticles of same material (1) through the solvent (3) and can be determined from the pure component [Eq. (3)]:

$$A_{131} = (\sqrt{A_{11}} - \sqrt{A_{33}})^2 \quad (3)$$

where, A_{11} = Hamaker constant for pure gold (4×10^{-19} J)^[33] and A_{33} was obtained from the Lifshitz theory following the relation [Eq. (4)]:^[34]

$$A_{33} = \frac{3}{4} k_B T \left(\frac{\epsilon_3 - \epsilon_{vac}}{\epsilon_3 + \epsilon_{vac}} \right)^2 + \frac{3h\nu_e}{16\sqrt{2}} \frac{(n_3^2 - n_{vac}^2)^2}{(n_3^2 + n_{vac}^2)^{3/2}} \quad (4)$$

where ϵ is the dielectric constant, n is the refractive index, k_B is Boltzman's constant, T is the temperature, h is Planck's constant and ν_e is main absorption frequency, typically 3×10^{15} s⁻¹. The values for ϵ_{vac} and n_{vac} are considered to be 1, while ϵ_3 and n_3 were obtained from the literature.^[34,35] From Eq. (4), the A_{131} for gold in scCO₂ was calculated at different pressures

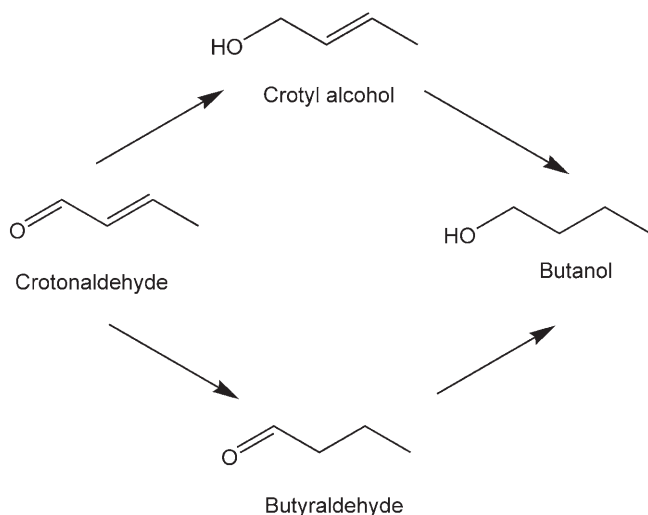
from 7 MPa to 17 MPa at 70°C and results are shown in Table 1. It has been observed that the Hamaker constant decreased from 2.345 eV to 1.465 eV with the increase in CO₂ pressure (density). According to the DLVO (Derjaguin–Landau–Verwey–Overbeek) theory, the Hamaker constant is proportional to the van der Waals attraction. On the other hand, the van der Waals attractive forces (Φ_{vdw}) between particles increase with the square of the ratio of the particle radius and are inversely proportional to the center-to-center separation distances. Therefore, the significant decrease of the Hamaker constant with the increase in CO₂ pressure leads to lower Φ_{vdw} and consequently to the increase in separation distance, which corresponds well with the smaller core-core interaction for the smaller particles obtained at higher pressures. To the contrary, the Φ_{vdw} increases with the increase in the particle size, the largest nanoparticles are obtained at lower solvent density conditions.

We have elucidated the pressure/density dependence of nanoparticle formation in scCO₂. We will now try to unravel the van der Waals forces between nanoparticles and silica surface. The Hamaker constant A_{132} for a gold particle (1) and silica surface (2) across the scCO₂ medium (3) may be given as follows [Eq. (5)]:^[34]

$$A_{132} = (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}}) \quad (5)$$

where A_{22} and A_{33} are the Hamaker constants of the silica surface and CO₂, respectively, obtained from the Lifshitz theory as described in Eq. (4). The values of A_{11} for gold,^[33] ϵ (3.91) and n (1.45) were taken from the literature.^[36,37] The strong pressure-dependent Hamaker constant demonstrates the ability to describe adsorption of the nanoparticles into the channels of the mesoporous silica support in the compressed fluid medium. The Hamaker constant for the gold-silica interaction decreases (0.858 eV to 0.291 eV) considerably with the increase in the CO₂ pressure from 7 to 17 MPa. Accordingly, when the dispersed particles are much smaller than the sizes of the pores, they might be only partially bonded to the pore walls.^[38] and any effect from the stiff surroundings cannot take place. However, when the particle size is large enough, the silica matrix would exert a great effect on the enclosed particles,^[39] the large A_{132} at lower pressure of CO₂ explains this phenomenon well. Therefore, the strong density dependence of A_{132} can be used as a probe to correlate the particle mobility and channel accessibility of the nanoparticles.

The catalytic activity of the Au-MCM-48 was tested by the selective hydrogenation of crotonaldehyde (Scheme 1) in scCO₂ medium. Figure 6 panels a and 6 show the results of Au-MCM-48 (10 MPa) and Au-MCM-48 (17 MPa), respectively. Under the studied



Scheme 1. Hydrogenation of crotonaldehyde in supercritical carbon dioxide.

reaction conditions [$P(\text{H}_2)=4$ MPa; temperature = 50°C ; reaction time = 4 h] the hydrogenation reaction path from crotonaldehyde to crotyl alcohol was more active than the formation of butyraldehyde. The selectivity to the crotyl alcohol increases with an increase in pressure from 7–14 MPa and then decreases. The change in selectivity along with CO_2 pressure can be correlated well with the density of the medium. The true reason for this effect may be a debatable issue, but there is no doubt that the pressure effect has a strong influence on the selectivity. On the other hand, it has been observed that the hydrogenation of crotonaldehyde in scCO_2 medium is sensitive to particle size. For instance, the selectivity to the crotyl alcohol decreases from ca. 90 % to ca. 50 % as the gold particle size changes from 10 nm [Au-MCM-48 (10 MPa)] to <2 nm [Au-MCM-48 (17 MPa)]. Bailie et al.^[40] studied the influence of particle size (4 nm to 20 nm) on the selectivity in the Au/ZnO system and proposed that the active site for the selective hydrogenation of crotonaldehyde to crotyl alcohol was associated with

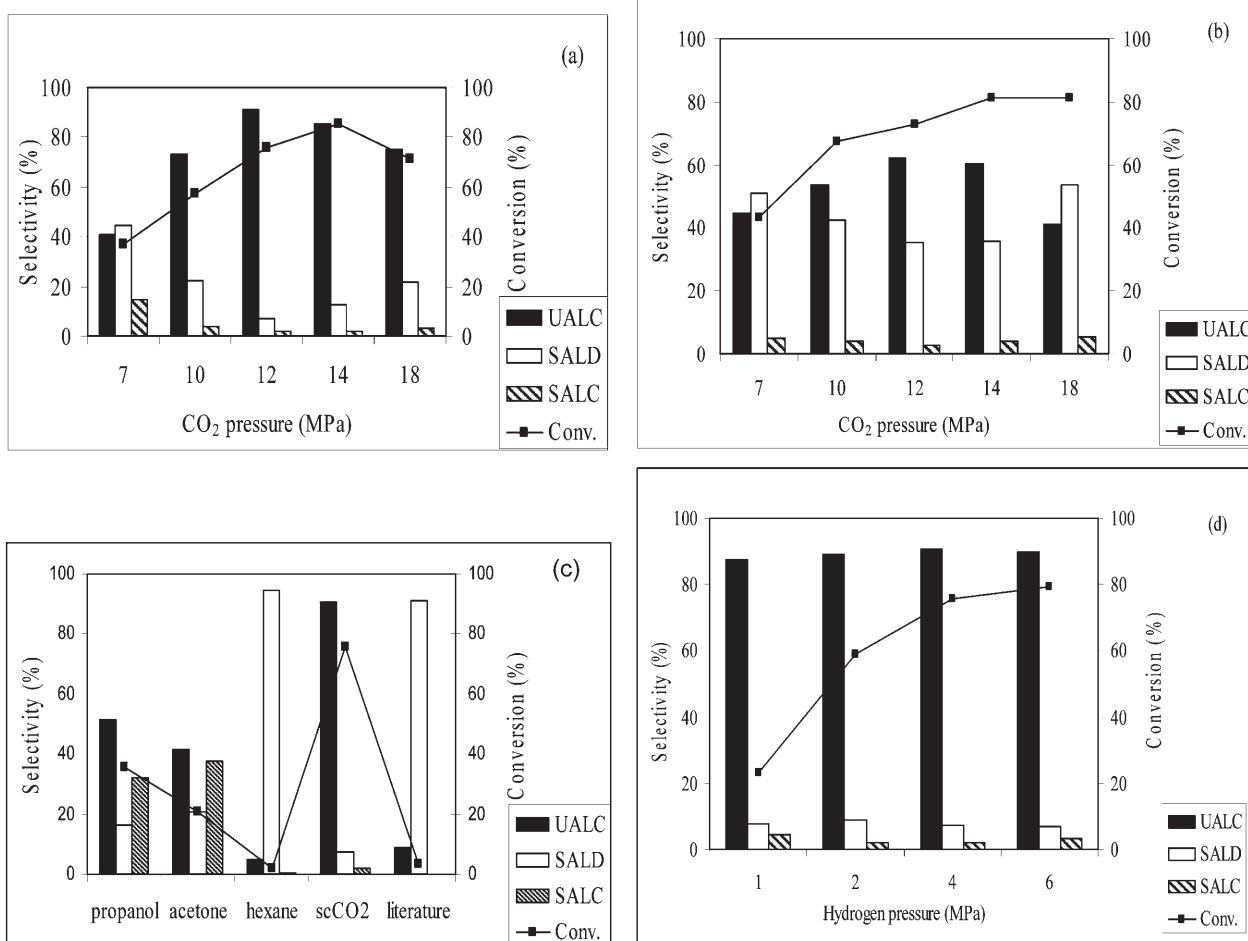


Figure 6. CO_2 pressure dependence on conversion and selectivity of crotonaldehyde hydrogenation using (a) Au-MCM-48 (7 MPa) and (b) Au-MCM-48 (17 MPa) in scCO_2 at fixed pressure of H_2 (4 MPa) and (c) comparison with organic solvent and literature data.^[43] (d) Effect of hydrogen pressure on conversion and selectivity.

the presence of larger gold particles. Moreover, for smaller gold particles, it is likely that a marked change in the electronic character of nanosized gold particles occurs with the change in the particle size and that the structure sensitivity originates from a quantum-size effect.^[41] The literature data regarding^[42,43] crotonaldehyde hydrogenation in conventional solvents revealed that the silica support does not favor the formation of crotyl alcohol. However, in our previous work^[44,45] it was found that the C=O hydrogenation was favored in scCO₂ medium compared to the conventional organic solvent. The catalytic activity of the synthesized materials indicates that the pores are still accessible for the reactant molecule after gold incorporation. This is in good agreement with the result obtained by N₂ adsorption-desorption analysis.

To compare the conversion and crotyl alcohol selectivity of Au-MCM-48 (10 MPa), we have carried out the same reaction in conventional organic solvents and the result is shown in Figure 6, panel c. Although the conversion and selectivity in the organic solvent were lowered compared to the scCO₂, they are still higher than with the Au/SiO₂ catalyst obtained by the chemical vapor deposition method.^[43] The occurrence of metal leaching was not observed, which is absolutely undesirable for a true heterogeneous catalyst.

The hydrogen pressure dependence study over Au-MCM-48 (10 MPa) revealed that the highest selectivity of crotyl alcohol was obtained at 4 MPa of hydrogen (Figure 6, panel d). The high solubility of hydrogen in scCO₂ increases the conversion along with the increase in hydrogen pressure. The product distribution for the crotonaldehyde hydrogenation is independent on the studied temperature. The reactions were conducted at 25°C, 35°C, 50°C and 80°C at 12 MPa of CO₂ with the constant hydrogen partial pressure of 4 MPa using Au-MCM-48 (10 MPa) because the high selectivity to the crotyl alcohol was obtained with Au-MCM-48 (10 MPa). With an increase in temperature, the conversion of crotonaldehyde increases, while the product selectivity remains constant.

A typical recycle experiment for the hydrogenation of crotonaldehyde showed that the catalyst is truly stable even after 5 recycles without losing its activity and selectivity. Elemental analysis for Au was done by ICP before and after recycling, and indicates <0.02% of Au leaching, confirming negligible leaching of gold from the catalyst. The reaction mixture was also tested after separation from the solid catalyst; it was inactive, further supporting that the leaching of gold is negligible. Au-MCM-48 obtained from CO₂ medium was highly stable and can be recycled several times without losing activity and selectivity.

Conclusions

A successful approach to the formation of gold nanoparticles into the channels of mesoporous material in scCO₂ medium using a hydrogen reduction technique is reported. It was possible to control the desired particle size by simple tuning of the solvent density, without disturbing the mesoporous structure. The variation of particle size with CO₂ pressure can be correlated well with the Hamaker constant, consequently with van der Waals attractions. The CO₂ medium can act as an effective medium for the synthesis of gold nanoparticles because of its low polarizability. An N₂ adsorption-desorption isotherm study shows that the pore blockage in MCM-48 after gold nanoparticle incorporation is minimum and pores are accessible, which was supported by the Hamaker constant between the silica surface and the gold core mediated by scCO₂. The catalytic activity provides conclusive evidence that the particles are inside the pores and are available for the reactant molecules. Therefore, the method described here is simple, reproducible and convenient. It will surely open a new trend for the synthesis of gold nanoparticle of desired size by tuning the solvent properties in a "green" and clean medium.

Experimental Section

Materials

Tetraethyl orthosilicate (TEOS) as the silica source and sodium hydroxide were purchased from Wako Pure Chemicals. Cetyltrimethylammonium bromide (CTAB) and HAuCl₄ were from Aldrich Chemical Co. All materials were used as received. CO₂ (>99.99%) was provided by the Nippon Sanso Co., Ltd.

Synthesis of MCM-48

The MCM-48 mesoporous silica was obtained by the procedure described in the literature.^[46] Typically, CTAB and sodium hydroxide were added to deionized water and stirred until they dissolved. After that, TEOS was added slowly under stirring conditions. The molar composition of the resultant gel was 1 M TEOS:0.25 M Na₂O:0.65 M C₁₆H₃₃-(CH₃)₃NBr:0.62 M H₂O. The final gel was autoclaved with heating at 140°C for 2 days. The solid product was filtered and washed thoroughly, followed by oven drying at 60°C. Finally, the product was calcined at 550°C for 8 h in air.

Synthesis of Gold Nanoparticles in scCO₂ Medium

The synthesis of gold containing MCM-48 (referred to as Au-MCM-48 in the text) in scCO₂ medium was conducted in a 50 mL stainless steel autoclave. In a typical experiment, 5 g of calcined mesoporous support and 10 mL of HAuCl₄ solution were loaded in the reactor before it was sealed. The closed reactor was placed in a constant temperature circulating oven of 70 °C and allowed to equilibrate. After the thermal equilibrium was reached, H₂ was introduced in the reactor and pressurized to 2.0 MPa. Then the reaction vessel was charged with CO₂ to the desired pressure using a high pressure syringe pump (JASCO scf-bpg). The vessel contents were mixed mechanically using a magnetic stirrer. The reaction was allowed to proceed for 2–4 h. During the synthesis, a back-pressure regulator maintained the constant reaction pressure. After the reaction, the reactor was placed in ice-cold water and depressurized very slowly and carefully. The samples were recovered from the container, dried at room temperature followed by the characterization.

Characterization Methods

The powder X-ray diffraction pattern was recorded on a Rigaku RAD-X system using monochromatized Cu K α radiation ($\lambda = 1.542 \text{ \AA}$). In general, the diffraction data were collected using the continuous scan mode with a scan speed of 2 deg/min over the scan range $2\theta = 1.5\text{--}15^\circ$ and for wide-angle ($2\theta = 30\text{--}70^\circ$) measurements. Transmission electron microscopy (TEM) of the material was performed on a Philips Technai operating at 200 kV. The powder was suspended in ethanol by an ultrasonic method. A drop of this solution was placed on the grid with a holey carbon/copper film and then allowed to dry, covered by a watch glass. N₂ adsorption-desorption isotherms were obtained at -196°C with a Micromeritics ASAP 2000 instrument. The sample was first outgassed at 300°C for 24 h immediately prior to data collection. The volume of the adsorbed N₂ was normalized to standard temperature and pressure. The surface area and the pore size distribution were calculated by applying the BET equation^[47] and BJH formula from the adsorption branch of the isotherm,^[48] respectively, to avoid the presence of artificial maxima on the pore size and other undesirable effects.^[49] The UV-Vis spectra of the materials were recorded on a Shimadzu spectrophotometer operating in the reflection mode at a resolution of 2 nm using aluminum oxide as standard. The FT-IR spectrum in the framework region (1300 cm^{-1} to 400 cm^{-1}) was recorded on a Horiba FT-720 using a KBr pellet. About 1 mg of finely powdered sample was mixed with 300 mg of dried KBr and then pressed to obtain the pellet.

Catalytic Activity

The hydrogenation of crotonaldehyde was carried out in a stainless steel batch reactor (50 mL) in scCO₂ medium.^[50] 100 mg of the catalyst and 6.5 mmol of the reactant were loaded into the reactor which was placed in an oven at a

temperature of 50°C . The reactor was sealed and flushed with 2 MPa of CO₂ for 3–4 times to remove the air and kept for 90 min to attain a constant temperature. A prescribed amount of hydrogen was first introduced into the reactor. After that, liquid CO₂ was charged using a high-pressure syringe pump, and then compressed to the desired pressure. A back-pressure regulator was used to maintain the constant pressure of the system. The reaction was conducted while stirring the mixture with a magnetic stirrer for 2 h. The reactor was then cooled to room temperature with an ice bath and depressurized to atmospheric pressure. Finally, the liquid product was separated from the catalyst by filtration then identified by GC/MS and analyzed quantitatively by GC (HP 6890) equipped with flame ionization detector. Quantification of the products was obtained by a multipoint calibration curve for each product.

The stability of the heterogeneous catalyst was evaluated by recovering it from the hot reaction mixture (temperature 50°C) by filtration and analysis by ICP-AES. On the other hand, the filtrate has been used in a new reaction but no catalytic activity was observed.

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