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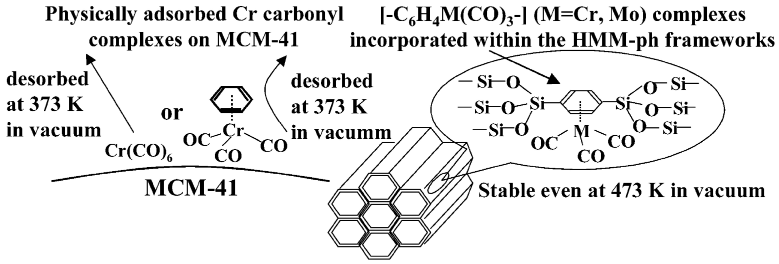

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Preparation and Characterization of Unique Inorganic−Organic Hybrid Mesoporous Materials Incorporating Arenetricarbonyl Complexes [$-C_6H_4M(CO)_3-$] (M = Cr, Mo)

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In recent years, many studies have been devoted to the synthesis of inorganic−organic hybrid porous materials and their various applications.[1] The development of functional hybrid mesoporous materials (HMM) containing organic moieties, such as $-C_2H_4-$,[2,3] $-C_2H_2-$,[3,4] and $-C_6H_4-$[5], within the silica framework has attracted much attention for their potential in the fields of catalysis and separation chemistry. At present, HMMs functionalized by the addition of a sulfuric acid group have been applied in solid acid catalysts for esterification reactions.[5−7] Another approach is the incorporation of organometallic complexes within the HMM framework, although there are yet few studies on this. The present study deals with the successful incorporation of arenetricarbonyl complexes [$-phM(CO)_3-$] (ph = C_6H_4; M = Cr, Mo) within the organosilica framework of phenylene ($-C_6H_4-$)-bridged HMM (HMM-ph) by a simple chemical vapor deposition (CVD) method. The incorporation of variations of an arenetricarbonyl complex within the HMM framework and their stability under thermovacuum treatment were investigated by FT-IR and UV−vis analyses.

HMM-ph were synthesized by a method reported by Inagaki et al.[5] using 1,4-bis(triethoxysilyl)benzene and octadecyltrimethylammonium chloride. Inorganic siliceous MCM-41 was synthesized using fumed silica and cetyltrimethylammonium bromide as precursors.[8] HMM-ph incorporating arenetricarbonyl complexes, HMM-phM(CO)$_3$, was prepared by CVD treatment of HMM-ph with $Cr(CO)_6$ at 398 K or $Mo(CO)_6$ at 348 K for 40 min in vacuum. MCM-41 deposited with $Cr(CO)_6$ or $C_6H_6Cr(CO)_3$ (denoted as Cr(CO)$_6$/MCM-41 and $C_6H_6Cr(CO)_3$ /MCM-41) were prepared at 398 and 343 K, respectively, by a physical vapor deposition (PVD) method for 40 min in vacuum. Prior to the introduction of the metal carbonyl compounds, HMM-ph and MCM-41 were degassed at 473 K for 2 h. After CVD or PVD treatment, the samples were transferred to the cells for FT-IR and UV−vis measurements under nitrogen, and spectral measurements were carried out in vacuum at 298 K.

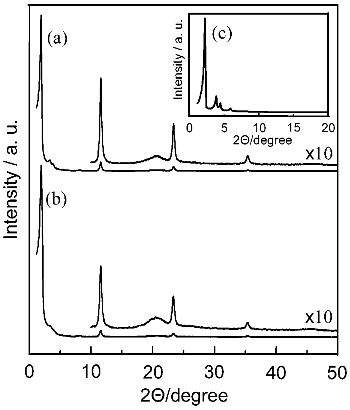

Figure 1. XRD patterns of (a) HMM-ph, (b) HMM-phCr(CO)$_3$, and (c) MCM-41 measured at 298 K in air.

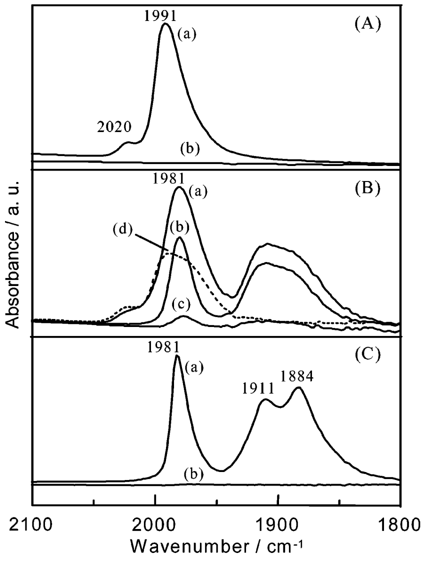

Figure 2. FT-IR spectra of (A, a) Cr(CO)$_6$/MCM-41, (B, a) HMM-phCr(CO)$_3$, (B, d) HMM-ph deposited with $Cr(CO)_6$ at 353 K, and (C, a) $C_6H_6Cr(CO)_3$/MCM-41, and the effects of the evacuation temperature on the FT-IR spectra (A, b; B, b−c; C, b). Evacuation temperature: (A, b) 373 K; (B, b) 473 K; (B, c) 503 K; (C, b) 373 K. All spectra were recorded as the difference in the spectrum before and after CVD or PVD treatment.

Figure 1 shows the XRD patterns of HMM-ph, HMM-phCr(CO)$_3$, and MCM-41. HMM-ph shows three XRD peaks ($d = 44.6$, 25.2, 21.8 Å) in the region of $2\theta < 10°$ due to a two-dimensional hexagonal structure with a lattice constant $a_0 = 51.5$ Å. Moreover, HMM-ph exhibits additional small sharp peaks ($d = 7.6$, 3.8, 2.5 Å) in the region of $10° < 2\theta < 50°$, showing that the periodicity of the $O_{1.5}Si-C_6H_4-SiO_{1.5}$ units exists within the wall of the mesoporous framework, although the wall crystallinity is rather low compared to previous reports.[5] As shown in Figure 1b, the XRD pattern of HMM-phCr(CO)$_3$ scarcely changed from that of HMM-ph, indicating that the mesoporous structures as well as the molecular scale periodicity were maintained even after CVD treatment of HMM-ph with $Cr(CO)_6$ at 398 K. The XRD pattern of MCM-41 exhibited four typical peaks ($d = 38.7$, 22.5, 19.6, 14.6 Å) in the region of $2\theta < 10°$ due to a two-dimensional hexagonal structure ($a_0 = 44.7$ Å). The BET surface areas of HMM-ph and HMM-phCr(CO)$_3$ were estimated at 806 and 771 m^2/g, respectively.

Figure 2A (a) shows the FT-IR spectrum of Cr(CO)$_6$/MCM-41, and the peaks observed at 1991 and 2020 cm^{-1} were assigned to

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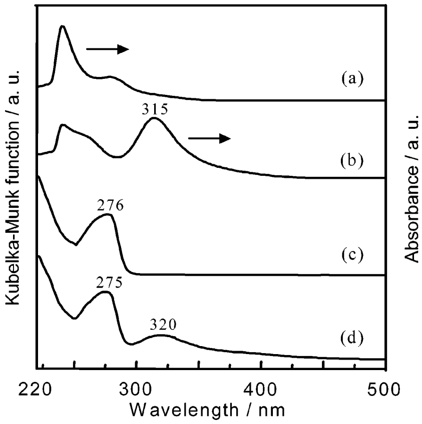
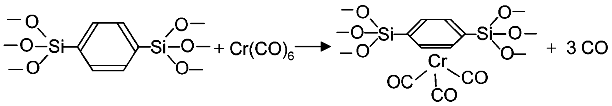


Figure 3. (a, b) Transmission and (c, d) diffuse reflectance UV−vis spectra of (a) $Cr(CO)_6$ in chloroform, (b) $C_6H_6Cr(CO)_3$ in chloroform, (c) HMM-ph, and (d) HMM-ph$Cr(CO)_3$.

the T_{1u} and E_g vibrational modes, respectively, of the physically adsorbed $Cr(CO)_6$ on the amorphous SiO_2 surface.[9] As shown in Figure 2B (a), the FT-IR spectrum of HMM-ph$Cr(CO)_3$ is quite different from that observed for $Cr(CO)_6$/MCM-41, with one sharp peak at 1981 cm^{-1} and broad peak at 1940−1840 cm^{-1}. These two bands correspond well to the a_1 (1981 cm^{-1}) and e (1911, 1884 cm^{-1}) vibrational mode of the physically adsorbed $C_6H_6Cr(CO)_3$ on the amorphous SiO_2 surface (Figure 2C (a)).[9] These results clearly indicate that arenetricarbonyl complexes [−ph$Cr(CO)_3$−] are formed by the reaction of $Cr(CO)_6$ with the phenylene moieties of HMM-ph, accompanied by the evolution of CO (eq 1).



(1)

The evolution of CO during CVD treatment was confirmed by GC analysis. The difference in the splitting of the e vibrational mode (1940−1840 cm^{-1}) observed for HMM-ph$Cr(CO)_3$ and C_6H_6-$Cr(CO)_3$/MCM-41 can be ascribed to the different perturbations in the local structure of the chromium carbonyl complexes from an ideal C_{3v} symmetry.[9] The Cr loading of HMM-ph$Cr(CO)_3$ was determined at 3.9 wt % as Cr metal by atomic absorption analysis, which showed that 15.0% of the phenylene moieties within HMM-ph was transferred into the arenetricarbonyl complexes. It should be noted that the FT-IR spectrum of HMM-ph deposited with $Cr(CO)_6$ at 353 K (Figure 2B (d)) shows two peaks due to the physically adsorbed $Cr(CO)_6$ at 2020 and 1991 cm^{-1}, suggesting that the preparation of HMM-ph$Cr(CO)_3$ requires CVD treatment above 353 K.

The thermal stability of HMM-ph$Cr(CO)_3$ was also investigated, and the −ph$Cr(CO)_3$− complexes within HMM-ph$Cr(CO)_3$ were found to exist stably even under thermovacuum treatment at 473 K and to decompose at a temperature range between 473 and 503 K (Figure 2B). However, $Cr(CO)_6$ or $C_6H_6Cr(CO)_3$ deposited on MCM-41 completely desorbed as low as 373 K in vacuum (Figure 2A,C). Although only a few studies have been carried out on the synthesis of nonordered amorphous organosilica gels, including arene metal carbonyl moieties by wet processes using organic solvents,[10] here, the direct and stable incorporation of arene metal carbonyl complexes within highly ordered hybrid mesoporous materials could be achieved by applying simple CVD treatments.

Figure 3 shows the UV−vis spectra of HMM-ph, HMM-ph$Cr(CO)_3$, and chloroform solutions of $Cr(CO)_6$ and $C_6H_6Cr(CO)_3$. An intense band at around 276 nm for HMM-ph can be assigned to the $\pi-\pi^*$ transition of the framework phenylene moieties,[11] while the band at around 315 nm and long-tailed absorption beyond 400 nm for $C_6H_6Cr(CO)_3$ can be assigned to a charge-transfer band from Cr to the benzene ring and the ligand field absorption of Cr, respectively.[12] However, $Cr(CO)_6$ exhibits no strong absorption band above 300 nm. The UV−vis spectrum of HMM-ph$Cr(CO)_3$ involves the superimposed absorption of both HMM-ph and $C_6H_6Cr(CO)_3$, confirming the formation of arenetricarbonyl complexes [−ph$Cr(CO)_3$−] within the framework of HMM-ph. Furthermore, HMM-ph$Cr(CO)_3$ was found to exhibit typical Cr2p XPS peaks for $C_6H_6Cr(CO)_3$ (Cr2$p_{1/2}$, 586.0 eV; Cr2$p_{3/2}$, 576.5 eV), confirming the formation of −ph$Cr(CO)_3$− complexes.[13]

It should be noted that the incorporation of Mo carbonyl complexes (−ph$Mo(CO)_3$−) within HMM-ph can also be achieved by the simple CVD treatment of HMM-ph with $Mo(CO)_6$ at 348 K. In fact, thus prepared HMM-ph$Mo(CO)_3$ exhibits typical FT-IR bands at 1984 and 1940−1840 cm^{-1} due to $C_6H_6Mo(CO)_3$,[14] and these bands were found to exist stably even under thermovacuum treatment at 523 K (data not shown).

In summary, highly ordered HMM incorporating arenetricarbonyl complexes has been successfully developed by a simple CVD method, and a high thermal stability has been achieved. This novel HMM can be utilized in the development of unique heterogeneous catalysts since arenetricarbonyl complexes exhibit effective catalytic activity for such reactions as the hydrogenation of polyunsaturates into cis-unsaturated products.[15] HMM-ph$Cr(CO)_3$ also can undergo various transformations of their arene moieties due to high electron-withdrawing ability and stereocontrol effect caused by the $Cr(CO)_3$ moieties,[16] which can be applied for the preparation of various functionalized hybrid mesoporous systems.

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Note Added after ASAP Publication. After this paper was published ASAP on November 11, 2005, a typographical error in the last sentence of the text was corrected. The corrected version was published ASAP November 14, 2005.

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