UV Raman Spectroscopy for Characterization of Chromium Species on Cr-MCM-41

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UV Raman spectroscopy could distinguish the chromate species on Cr-MCM-41. Only one kind of monochromate species was observed on the Cr-MCM-41 synthesized by a direct hydrothermal synthesis method whereas several types of chromate species possibly including both monochromates and polychromates existed on that synthesized by a template-ion exchange method.

Supported chromium oxide was used for the dehydrogenation of propane or isobutane to produce propylene or isobutene.[1,2] Many chromium-containing compounds were also studied as catalysts in the selective oxidation of various organic substrates.[2,3] Several chromium species such as isolated monochromate, polychromate, and Cr_2O_3 clusters were reported to exist on supported catalysts and behaved differently in various catalytic reactions.[2–5] Because of the large surface area of MCM-41, Cr-containing MCM-41 may possess high concentration of isolated chromium species which may be crucial for selective catalytic reactions.[6–9] For example, Cr-containing mesoporous molecular sieves exhibited high reactivity for several photocatalytic reactions;[10] Cr-MCM-41 showed higher activity and stability for the liquid phase oxidation than Cr-containing microporous materials and pillared clays.[11,12] So far, UV-Vis spectroscopy has mainly been used for the characterization of chromium species existing in MCM-41.[6–12] Both monochromate and polychromate species may possibly exist on the surface of Cr-MCM-41 after calcination. Raman spectroscopy may be a powerful tool to distinguish these species. Raman spectrum of Cr-MCM-41 with visible laser line as exciting source was once reported,[8] but we recently found that the serious fluorescence affected the background and only lower signal to noise was obtained. It has been shown that the use of UV-Raman spectroscopy can avoid fluorescence interference from molecular sieves or related materials.[13] In this communication, for the first time, we apply UV-Raman spectroscopy to investigate the chromium species introduced to MCM-41.

Cr-MCM-41 was prepared by two different methods, i.e., direct hydrothermal synthesis (DHT) and template ion exchange (TIE) methods. We have used these two methods for the syntheses of V-,[14] Fe-,[15] and Mn-MCM-41[16] and have shown that different method leads to different location and structure of metal cations and different catalytic properties. For the DHT synthesis, chromium nitrate, sodium silicate and hexadecyltrimethylammonium bromide were used as the sources of chromium, silicon and the template, respectively. After hydrothermal synthesis at 150 °C for 48 h, the resultant solid was washed with deionized water, dried at 40 °C in vacuum and finally calcined at 550 °C for 6 h. In the TIE preparation, chromium was introduced by exchanging the template cations embraced in the uncalcined MCM-41 with the Cr^{3+} ions in aqueous solution at 80 °C, followed by washing, drying and calcination. For comparison, Cr/Cab-O-Sil was prepared by a conventional impregnation method. All the samples were characterized by XRD, N_2 adsorption (77 K), diffuse reflectance UV-vis and Raman spectroscopic measurements. UV-Raman measurements were carried out with a Renishaw UV-Vis Raman System 1000R using the UV line at 325 nm from a Kimmon IK3201R-F He-Cd laser as the exciting source. The sample was loaded in an in situ cell and was treated in pure N_2 gas flow at 200 °C for dehydration. A laser output of 30 mW was used and the maximum incident power at the sample was approximately 6 mW.

XRD measurements showed that four diffraction lines at 2θ degrees of 2–6 ascribed to (100), (110), (200), and (210) of the hexagonal regularity of MCM-41 were observed for the Cr-MCM-41 samples synthesized by both the DHT and TIE methods with Si/Cr ratio larger than 25. The increase in Cr content to 3.4 wt% (Si/Cr = 25) remarkably decreased the peak intensity. Narrow pore size distribution around 2.5–3.0 nm was obtained from N_2 adsorption measurements for all the samples. The surface area and pore volume gradually decreased with an increase in Cr content up to 1.7 wt% (Si/Cr = 50) and became remarkably low for the sample with Si/Cr ratio of 25 for both the DHT and TIE samples. These results indicate the decrease in structural regularity at high Cr content for both series samples.

The color of all the as synthesized Cr-MCM-41 samples was pale green and it changed to pale yellow after calcination. This suggests the change of the oxidation state of Cr species probably from Cr^{3+} to chromate with Cr^{6+} after calcination. Figure 1 shows the diffuse reflectance UV-Vis spectra of Cr-MCM-41 synthesized by both the methods. UV bands at 280 and 370 nm, which could be assigned to O-Cr(VI) charge transfers of chromate species, were mainly observed for both types of the samples. Although a weak shoulder around 440 nm was observed for the TIE samples, the difference between the TIE and the DHT samples was not distinct since the large band at 370 nm may overlap the shoulder at 440 nm in the latter case.

We recorded Raman spectra of Cr-MCM-41 samples with visible laser at 514 nm as exciting source, but useful information was not obtained because of the serious fluorescence. Figure 2 shows the UV-Raman spectra of Cr-MCM-41 samples along with Cr/Cab-O-Sil and Cr_2O_3. The measurements were performed at 200 °C in N_2 gas flow to keep the sample dehydrated since it was clarified that the hydration of Cr-MCM-41 would greatly affect the Raman spectra. No interference of the fluorescence was observed in this case. As shown in Figure 2, an intense band at 980 cm^{-1} was observed for the Cr-MCM-41 synthesized by the DHT method, while a set of multi-bands around 1010–1100 cm^{-1} appeared in addition to that at 980 cm^{-1} for the TIE samples with the same Si/Cr ratio. Wachs and coworkers have studied a number

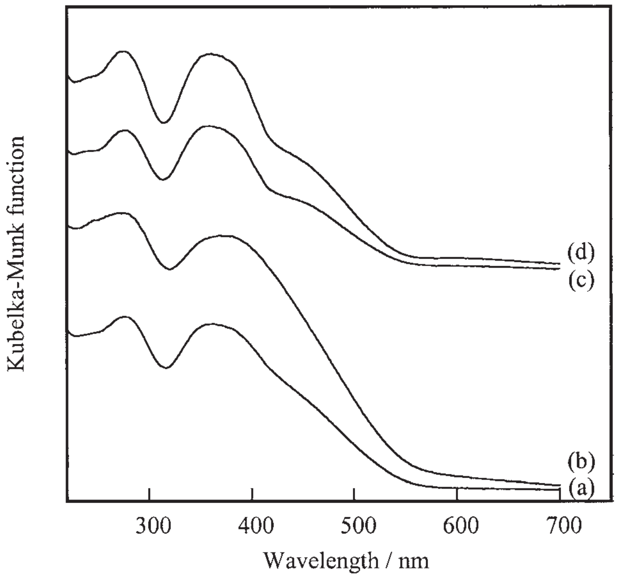

Figure 1. UV-Vis spectra of Cr-MCM-41. (a) Cr-MCM-41-DHT (Si/Cr = 50), (b) Cr-MCM-41-DHT (Si/Cr = 25), (c) Cr-MCM-41-TIE (Si/Cr = 100), (d) Cr-MCM-41-TIE (Si/Cr = 50).

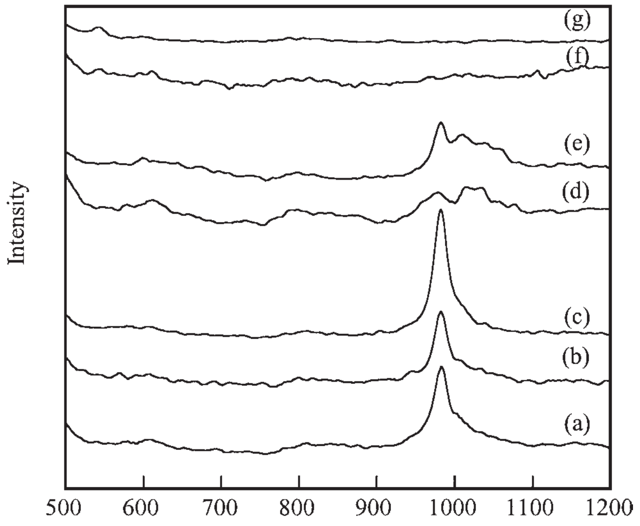

Figure 2. UV-Raman spectra of the Cr-MCM-41 along with Cr/Cab-O-Sil and Cr_2O_3. (a) Cr-MCM-41-DHT (Si/Cr = 100), (b) Cr-MCM-41-DHT (Si/Cr = 50), (c) Cr-MCM-41-DHT (Si/Cr = 25), (d) Cr-MCM-41-TIE (Si/Cr = 100), (e) Cr-MCM-41-TIE (Si/Cr = 50), (f) Cr/Cab-O-Sil (Si/Cr = 100), (g) Cr_2O_3.

of supported Cr oxides with Raman spectroscopy and suggested that the band at 980–990 cm^{-1} could be assigned to the Cr-O vibration stretching of dehydrogenated monochromate species (CrO_4^{2-}), and those at 1000–1010 cm^{-1} can be ascribed to the Cr-O stretching of dehydrated polychromate species.[2] Figure 2 clearly shows that only one kind of chromate species assignable to monochromate exists in the Cr-MCM-41 synthesized by DHT method, whereas the Cr-MCM-41 synthesized by TIE method contains several types of chromate species in addition to the monochromate at 980 cm^{-1}. We tentatively ascribed the multibands observed at 1010–1100 cm^{-1} to the dehydrated polychromates with different size, e.g, dichromate, trichromate and tetrachromate. It is worth mentioning that the chromium centers in both monochromate and polychromate species are tetrahedrally coordinated with oxygen.

It should be noted that Cr/Cab-O-Sil resembled Cr_2O_3, and no distinct Raman band except for a weak one at 548 cm^{-1} was observed in their UV-Raman spectra. This band can be assigned to the octahedral Cr^{3+} of Cr_2O_3. XRD measurements showed the appearance of the diffraction peaks belonging to Cr_2O_3 for Cr/Cab-O-Sil with Cr content higher than 1.7 wt% (Si/Cr = 50), while no peak of Cr_2O_3 was observed for all the Cr-MCM-41 samples with Cr content up to 6 wt%. Thus, different from the dispersed chromate species on Cr-MCM-41, chromium on Cr/Cab-O-Sil mainly aggregated as Cr_2O_3 clusters.

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