

A DRIFTS investigation on the decomposition mechanism of Mn Acetylacetonates supported on SBA-15

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Introduction

Synthesis of highly dispersed metal oxides catalyst is of great importance. The structure and dispersion depend primarily on the preparation method, nature of the support and the precursor. Ordered mesoporous materials with their intrinsically high surface areas are particularly suited for obtaining highly dispersed metals or metal oxides. There is a growing interest to replace traditional precursors such as chlorides, nitrates to synthesize of metals and metal oxides with metal acetylacetonates either in the presence or absence of oxygen [1-4]. The main reasons are to obtain uniform dispersion and formation of highly-dispersed nanoparticles. Generally, metal acetylacetonates are treated at high temperatures in the presence of oxygen/air in order to form the corresponding oxides. However, the detailed decomposition mechanism of supported metal acetylacetonates is not fully understood.

Experimental

The synthesis of SBA-15 was carried out as previously reported [5], using Pluronic P123 (BASF) surfactant as template and tetraethyl orthosilicate (TEOS, 98%) as silica source. Manganese (II) acetylacetonate ($[\text{CH}_3\text{COCH}=\text{C}(\text{O})\text{CH}_3]_2\text{Mn}$, Aldrich) (2.5 mmol/gram (SBA-15) were dissolved in acetone (C.P.) at room temperature, corresponding to ca. 13 wt% of Mn_3O_4 . SBA-15 powder was then added to the solution after manganese (II) acetylacetonate had been completely dissolved. The precursor was obtained by stirring the solution vigorously and then the solvent was evaporated completely. Subsequently, the precursor was washed with acetone. Finally, the precursor was calcined at 773 K for 5 h under air with a ramping rate of 1 K/min as previously described [6]. "in situ" DRIFTS analysis was carried out on a BIO RAD spectrometer equipped with an MCT detector and a high temperature DRIFTS cell fitted with KBr windows. Sample was loaded into the DRIFT cell without any further dilution. The spectra were acquired with a resolution of 4 cm^{-1} , typically averaging 150 scans. DRIFT spectra were taken at various temperatures ranging RT to $300\text{ }^\circ\text{C}$. The flow rate of both gases was controlled using thermal mass flow controllers.

Results and Discussion

MnO_x supported on mesoporous SBA-15 catalysts have been prepared by molecularly designed dispersion method, using organic precursors of Mn(II) acetylacetonate and Mn(III) acetylacetonate. These materials were characterized by XRD, in situ DRIFTS, and Raman spectroscopy. XRD results suggest the formation of Mn_2O_3 and Mn_3O_4 phases on SBA-15 by thermolysis of Mn(III) acetylacetonate and Mn(II) acetylacetonate, respectively. The decomposition mechanism was studied by FT-IR technique using diffuse reflectance. The DRIFTS spectra recorded on Mn(acac)₂/SBA treated at different temperatures are shown in Figure 1. The sharp band at 3745 cm^{-1} can be assigned to isolated silanol groups on pure SBA-15 and the this band is slightly shifted to lower wavenumber after deposition of Mn (II and III) acetylacetonates. A very broad band in the region of $3600\text{-}3400\text{ cm}^{-1}$, assigned to bridged

silanol groups. The decrease of isolated -OH groups intensity suggest that acetylacetonate preferentially reacting with these groups to anchor on the surface. The appearance of the broad band in the region of $3600\text{-}3400\text{ cm}^{-1}$ suggests that Mn precursors are anchoring onto the surface via hydrogen bonding on SBA-15. It is interesting to note here that isolated silanol band reappears after treatment at high temperatures, indicating that these groups are partially restored upon decomposition of the acac precursor. Intensity of this band increased with temperature and oxidation of the sample for 3h. FTIR spectrum of Mn(acac)₂/SBA-15 sample shows the characteristic bands of acetylacetonate complexes in the region of $1200\text{ to }1600\text{ cm}^{-1}$. The intensity of the bands at $1385\text{ (}\nu\text{C-C and } \delta\text{C-H)}$ and $1525\text{ (}\nu\text{C=O)}$ cm^{-1} decreases as the treatment temperature is increased. After oxidation at $300\text{ }^\circ\text{C}$ only two bands remain at 1565 and 1445 cm^{-1} , respectively, which could be attributed to acacH adsorbed on SBA-15 (7). These bands suggest that Mn(acac)₂ decomposition mechanism taking place via ligand exchange between precursor and support by forming Hacac. Reappearance of the band at 3745 cm^{-1} , particularly at high temperatures further suggests the formation of Si-O-Mn.

Significance

This systematic study provides the details regarding the surface mechanism of the formation of MnO_x on SBA surface.

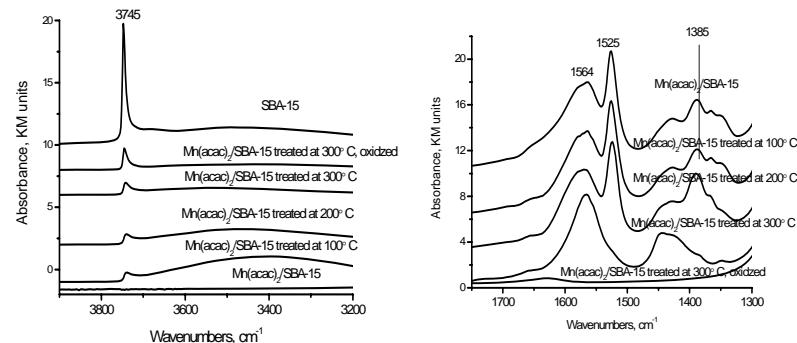


Figure 1. in situ DRIFTS spectra of Mn(acac)₂/SBA-15 treated at various temperatures A) DRIFTS spectra in the region of $3900\text{-}3200\text{ cm}^{-1}$, B) DRIFTS spectra in the region of $1800\text{-}1300\text{ cm}^{-1}$.

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