Surface state of molybdenum cations in MoO$_3$/CeO$_2$

DONG Lin, HU Jingqiu, XU Bin and CHEN Yi
Department of Chemistry, Institute of Mesoscopic Solid State Chemistry, Nanjing University, Nanjing 210093, China

Keywords: MoO$_3$, CeO$_2$, dispersion capacity, incorporation model, surface species.

STUDY on the surface interaction of supported catalysts is a fundamental subject in catalysis for their wide application in industrial reactions. In the past decades, deep investigation on the interaction between the active species and the supports, such as $\gamma$-Al$_2$O$_3$, SiO$_2$, TiO$_2$, ZrO$_2$, etc., has been carried out, and the properties of the supports as well as the roles of the supported active species at different states in the catalysis process have been further clarified$^{[1-3]}$. Recently, some novel catalysts, with rare-earth metal oxides as supports, have attracted much attention for their unique properties in the catalysis application, such as the reaction of CO + H$_2$ and the automobile exhaust emission control.

In this work, Mo(VI) is taken as an active species supported on CeO$_2$, XRD, laser Raman spectroscopy (LRS). Diffuse reflectance infrared (DR-IR) and ultra-violet diffuse reflectance spectroscopy (UV-DRS) are used to characterize the state of molybdenum in MoO$_3$/CeO$_2$. In consideration of the structure of the CeO$_2$ surface, the surface state of Mo$^{6+}$ species is discussed by an incorporation model. All the results in this study are in agreement with those obtained in some other systems, such as MoO$_3$/$\gamma$-Al$_2$O$_3$, WO$_3$/$\gamma$-Al$_2$O$_3$, NiO/$\gamma$-Al$_2$O$_3$ and ZnO/$\gamma$-Al$_2$O$_3$$^{[4]}$.

1 Experimental

BET surface areas of the samples were measured on a Micromeritics ASAP-2000 instrument equipped with a computer-controlled measurement system. XRD qualitative and quantitative analyses are carried out on a Shimadzu-XD-3A X-ray diffractometer by using CuK$\alpha$ radiation (0.514 18 nm) and Ni filter. LRS were recorded in air with a Spex Ramalog 1403 spectrometer equipped with a triple monochromator. The 488 nm line and laser source power of 200 mW were used. A laser power of 15—20 mW at the sample was applied. The scanning rate was 2 cm$^{-1}$·s$^{-1}$. DR-IR spectra were recorded on a Nicolet-510p FT-IR spectrometer with $\pm$ 2 cm$^{-1}$ resolution. DR-UV measurements were carried out on a UV-2100 ultra-violet
reflectance spectrometer. MgO power was used as a reference. Spectra were recorded from 190 to 700 nm.

CeO\textsubscript{2} was obtained by thermodecomposition of Ce(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O in air at a programmed temperature up to 550°C, at which CeO\textsubscript{2} was kept for 5 h, and the BET surface area was 73 m\textsuperscript{2}·g\textsuperscript{-1}. MoO\textsubscript{3} (AR) was supplied by Shanghai Chemical Reagent Company and pretreated at 420°C for 5 h before being used to prepare the samples. ZnO-modified CeO\textsubscript{2} (ZnO-CeO\textsubscript{2}) was prepared by impregnating 100 m\textsuperscript{2} CeO\textsubscript{2} support with 1.22 mmol Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, dried at 100°C to evaporate the excess water and then calcined at 450°C for 1 h; the BET surface area was 55 m\textsuperscript{2}·g\textsuperscript{-1}. MoO\textsubscript{3}/CeO\textsubscript{2} (or MoO\textsubscript{3}/ZnO-CeO\textsubscript{2}) samples with different Mo contents (X mmol MoO\textsubscript{3}/100 m\textsuperscript{2} support) were prepared by calcining the mixtures of MoO\textsubscript{3} and CeO\textsubscript{2} (or ZnO-CeO\textsubscript{2}) in air at 420°C for 24 h, respectively.

2 Results and discussion

2.1 Dispersion of MoO\textsubscript{3} on CeO\textsubscript{2}

In fig. 1 the peaks of the crystalline MoO\textsubscript{3}, 2\theta = 25.72° and 27.33°, disappeared for the calcined samples A′ and B′, in which Mo contents are 0.4 and 0.7 mmol/100 m\textsuperscript{2}, respectively. However, for sample C′, the peaks of crystalline MoO\textsubscript{3} still remain but the intensity decreases markedly by comparison of patterns (curve 1) and (curve 1′). The results show that, for the calcined samples, only surface Mo species exist for the low content sample and both surface Mo species and residual crystalline MoO\textsubscript{3} exist for the high Mo content sample. A further quantitative XRD result indicates that the dispersion capacity of MoO\textsubscript{3} supported on CeO\textsubscript{2} is 0.81 mmol/100 m\textsuperscript{2}.

In fig. 2 for the samples with Mo contents below the dispersion capacity, the bands at 800 and 963 cm\textsuperscript{-1} are evidently exhibited and the peak intensities for both of the bands grow from sample A, 0.4, to sample B, 0.7 mmol MoO\textsubscript{3}/100 m\textsuperscript{2}·CeO\textsubscript{2}. For the samples with the contents of 1.0 (C) and 1.4 (D) mmolMoO\textsubscript{3}/100 m\textsuperscript{2}·CeO\textsubscript{2}, the intensities of the two bands,