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Interaction of Oxygen and CH₄ with Molybdenum Oxide Catalysts

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Received June 16, 1997

The Near-Edge X-ray Absorption Fine Structure (NEXAFS) technique and Differential Scanning Calorimetry (DSC) were utilized to investigate the reaction of CH₄ and O₂ on the MoO₃/SiO₂ catalyst. The NEXAFS results showed that the stoichiometry of the molybdenum oxide catalyst supported on silica was MoO₃. MoO₃ was reduced to MoO₂ when the catalyst was exposed to CH₄ at 773 K. NEXAFS results confirm that lattice oxygen is directly related to the process of CH₄ oxidation which takes place on the surface of MoO₃/SiO₂ catalysts. DSC results show that the structure of MoO₃ changes around 573 K and this structural change seems to improve the migration of oxygen in the lattice.

Introduction

The MoO₃/SiO₂ catalyst is used for the partial oxidation of CH₄ to HCHO and CH₃OH.¹⁻³ Catalytic oxidation of methane to produce valuable hydrocarbons has been extensively studied.^{4,5} However, a lot of controversial results have been reported about the active species and reaction intermediates which are responsible for the partial oxidation of methane on the catalyst surface. One of the questions about catalytic oxidation of methane over MoO₃ is the role of lattice oxygen during the oxidation process. It has not been clearly determined whether lattice oxygen is directly related to the oxidation process. Isotopic labelling technique has been utilized to probe the origin of the oxygen species incorporated into reaction products.⁶ However, a definitive proof could not be obtained because of the isotopic exchange between the reaction products and labelled oxygen. In this paper, we will propose that lattice oxygen of MoO₃ takes part in the oxidation process of CH₄.

We utilized the Near-Edge X-ray Absorption Fine Structure (NEXAFS) technique and Differential Scanning Calorimetry (DSC) to investigate the MoO₃/SiO₂ catalyst. NEXAFS is a very powerful technique to investigate metal oxide surfaces. Among the capabilities of NEXAFS are: determination of chemical composition, the ability to detect the presence of specific bonds and determination of bond lengths of molecules, and the derivation of the precise orientation of molecules on surfaces or in solids.⁷ In the NEXAFS experiment, we detect both Auger electrons and fluorescence emission caused by X-ray absorption. Because we record both electron yield and fluorescence yield, the effect of surface charging can be minimized. Surface charging sometimes causes serious problems when the insulating material is analyzed using electron spectroscopy such as X-ray photoelectron spectroscopy. We will show that NEXAFS is an ideal technique for the study of insulating metal oxide ca-

talysts.

Experimental Methods

The MoO₃/SiO₂ catalysts were prepared by conventional pore volume impregnation technique using aqueous solution of high purity (NH₄)₆Mo₇O₂₄·4H₂O and silica gel. The surface area of silica gel was 300 m²/g and the pore volume was 1.15 cm³/g. After impregnation, the catalysts were dried at 120 °C for 10 hours and then calcined at 550 °C for 6 hours. Figure 1 shows the XRD profile of the MoO₃/SiO₂ catalyst prepared by this method. It clearly shows the orthorhombic structure when MoO₃ loading was 15% by weight. This implies that MoO₃ forms 3 dimensional particles on SiO₂. The particle size was estimated to be 330 Å based on

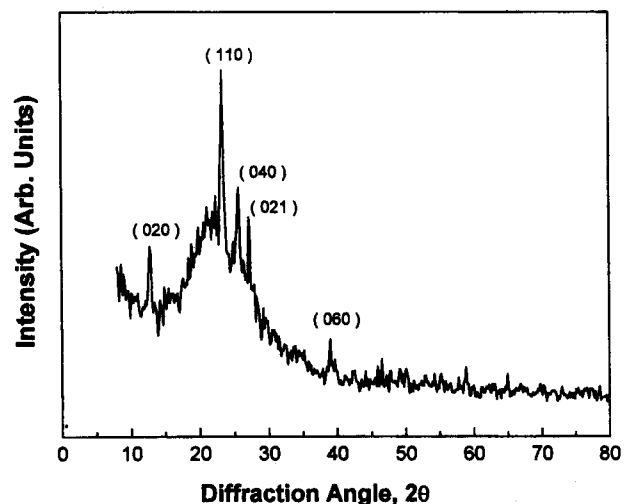


Figure 1. XRD pattern of MoO₃/SiO₂. MoO₃ loading on SiO₂ is 15% by weight.

line-broadening of diffraction lines.⁸ MoO_3 and MoO_2 powder samples were purchased from Aldrich and used for NEXAFS standards. The MoO surface was prepared by partially oxidizing the Mo foil in UHV.

The NEXAFS experiments reported here were carried out at the U1A beam line of the National Synchrotron Light Source, Brookhaven National Laboratory. The beam line is designed to perform both ultrahigh vacuum (UHV) investigation and the high-pressure reaction experiment. The NEXAFS spectra were taken by measuring the electron yield and fluorescence yield simultaneously. The beam line setup has been described in detail elsewhere.^{9,10} DSC profiles were obtained using Seiko DSC220C. The sample was always under oxygen environment during DSC experiments.

Results and Discussion

Figure 2 shows the electron-yield NEXAFS spectra of oxygen K-edge features of MoO_3 , MoO_2 and MoO . The oxygen K-edge spectrum of MoO_3 shows two major features at 530.5 eV and 533.5 eV. These features correspond to the transition of the oxygen 1s-orbital electron to molybdenum 4d-orbitals. Since the escape depth of electrons in this energy range is less than 10 Å,¹¹ the electron-yield NEXAFS spectrum provides the information about the first few monolayers of the surface. The dashed line of Figure 2 is the fluorescence-yield NEXAFS spectrum of MoO_3 . The fluorescence-yield spectrum represents the bulk property of solid because the mean-free path of photons in the energy range of this experiment is approximately 1500 Å in solid.¹² The electron- and fluorescence-yield spectra show quite similar fashion and which implies that the surface and bulk of MoO_3 have the same chemical composition.

Figure 2 compares the oxygen K-edge NEXAFS features of MoO_3 , MoO_2 and MoO . The relative intensity of 530.5 eV to 533.5 eV transition decreased as the oxidation state of Mo was changed from 6 to 2. This relative intensity

change is due to the change of the local structure of molybdenum oxides. These results demonstrate that the NEXAFS features of molybdenum oxides can be used as fingerprints to identify the stoichiometry of molybdenum oxide species on the surface.

The fluorescence-yield NEXAFS profile of MoO_3 supported on SiO_2 is shown in Figure 3. The oxygen K-edge energy of SiO_2 was higher than 535 eV and did not show any fine structures. The typical oxygen K-edge features of MoO_3 at 530.5 eV and 533.5 eV were clearly resolved from SiO_2 features. When one investigates insulating materials using electron spectroscopy such as ESCA, surface charging causes serious problems. Since we detect photons emitted from the sample in NEXAFS experiment, charging effect can be minimized. This is one of the advantages of the NEXAFS technique over other surface analysis tools. We did not have any surface-charging problem when we investigated MoO_3/SiO_2 samples using NEXAFS. The oxygen K-edge spectra of molybdenum oxides supported on silica clearly show that molybdenum oxide on SiO_2 has MoO_3 stoichiometry. This result agrees to XPS analysis results (XPS spectra are not shown).

We investigated the reaction of CH_4 and O_2 on the MoO_3/SiO_2 catalyst using NEXAFS. The catalyst of 15 wt% MoO_3/SiO_2 was placed in a high-pressure reaction chamber and the sample was exposed to 6 Torr of CH_4 for 10 minutes at 500 °C. Figure 4 shows the change of oxygen K-edge features of molybdenum oxide. The captured figure shows the whole spectrum of MoO_3/SiO_2 . Curve (a) is the untreated MoO_3/SiO_2 and Curve (b) is the CH_4 -treated MoO_3/SiO_2 . The intensity ratio of 530.5 eV to 533.5 eV feature decreased substantially after CH_4 treatment. This clearly indicates that MoO_3 was reduced by CH_4 . The stoichiometry of reduced molybdenum oxide cannot be determined exactly but it can be either MoO_2 or even less-oxidized molybdenum oxide.

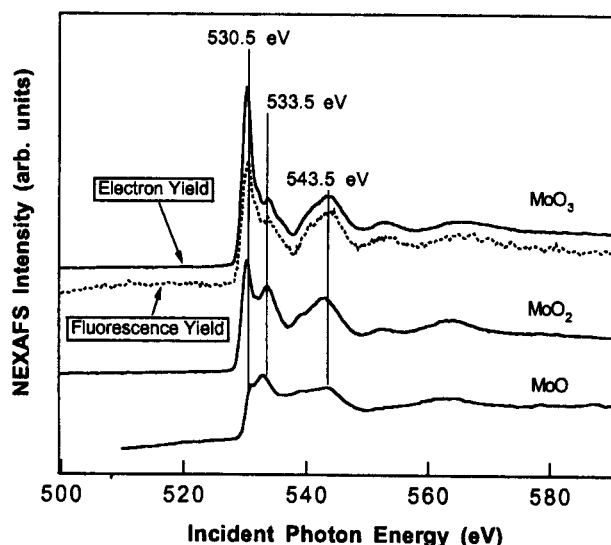


Figure 2. Comparison of NEXAFS spectra of MoO_x species. The spectra of solid line were obtained by recording the electron yield and the dashed-line spectrum was obtained by recording the fluorescence yield.

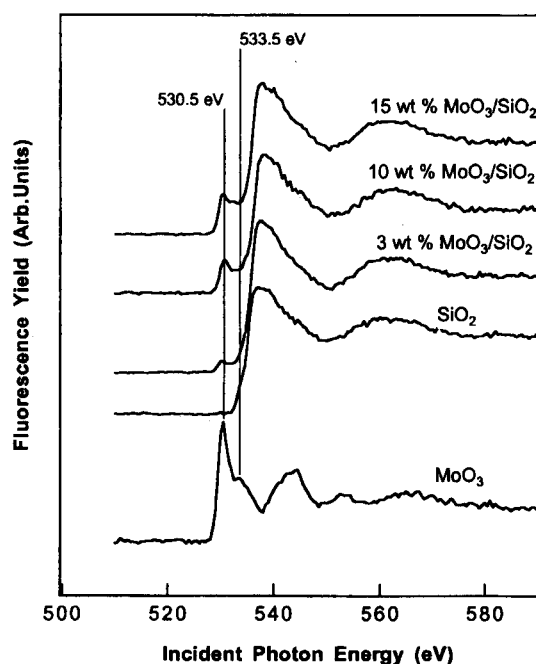


Figure 3. NEXAFS spectra of MoO_3 , SiO_2 , and MoO_3/SiO_2 .

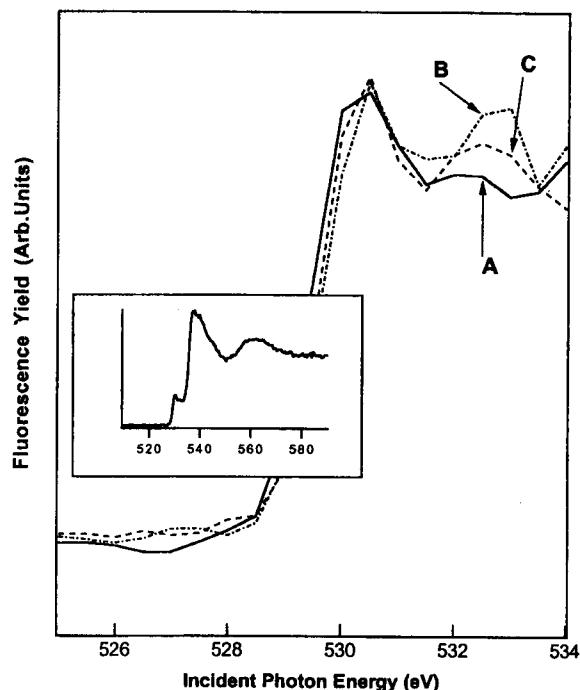


Figure 4. Change of the NEXAFS spectrum of $\text{MoO}_3/\text{SiO}_2$ after CH_4 and O_2 treatment. (a) $\text{MoO}_3/\text{SiO}_2$ catalyst, (b) the catalyst was exposed to 6 Torr of CH_4 for 10 minutes at 500°C , (c) the CH_4 -treated catalyst was exposed to 5 Torr of O_2 for 10 minutes at 300°C .

In this experiment, the NEXAFS spectra were obtained by monitoring the fluorescence yield. As it was mentioned earlier in this paper, the fluorescence-yield spectrum represented not the surface but the bulk property of the sample. This implies that lattice oxygen takes part in the methane oxidation process which takes place on the surface. So lattice oxygen should diffuse into the surface to react with CH_4 . Diffusion of lattice oxygen in the bulk and migration into the surface is discussed later in this paper.

The reduced molybdenum oxide catalyst was reoxidized after CH_4 oxidation reaction. It was exposed to 5 Torr of O_2 for 10 minutes at 300°C . Curve (c) in Figure 4 represents the oxygen K-edge feature of molybdenum oxide after reoxidation. In this oxidation condition, reduced molybdenum oxide was not completely oxidized to MoO_3 . However, the change of oxygen K-edge feature clearly shows that reduced molybdenum oxide was reoxidized even in this mild oxidizing environment.

Migration of oxygen in MoO_3 was studied using Differential Scanning Calorimetry (DSC). MoO_3 is an n-type semiconductor. Its conductivity decreases with an increase in oxygen pressure and varies from 10^{-8} ohm^{-1} at 20°C to 10^{-3} ohm^{-1} at 350°C .¹³ It is well known that molybdenum trioxide forms a lot of suboxides such as $\text{Mo}_{13}\text{O}_{38}$, Mo_9O_{26} , Mo_8O_{23} , and Mo_4O_{11} . There is a characteristic temperature for each compound, depending on the nature of the crystalline structure, at which the atoms or groups of atoms obtain the necessary mobility for changing their position. The movement of oxygen atoms creates oxygen vacancies and it is closely related to the change of the conductivity of MoO_3 .^{14,15}

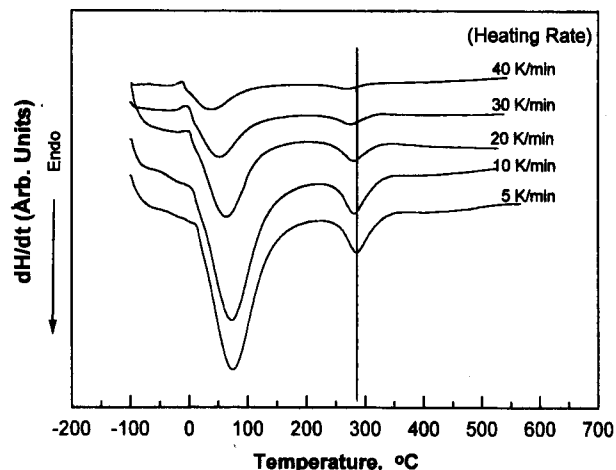


Figure 5. DSC profiles of the 15 wt% $\text{MoO}_3/\text{SiO}_2$ catalyst at various heating rates.

Figure 5 shows the DSC profiles of 7 wt% MoO_3 on SiO_2 at different heating rate under oxygen environment. Two endothermic peaks were observed. The first endothermic peak at 50 to 100°C represents desorption of H_2O from SiO_2 and MoO_3 . The second peak at 250 to 300°C is a characteristic peak for MoO_3 . This endothermic peak is related to the movement of oxygen atoms in the lattice of MoO_3 . This endothermic process seems to create the lattice structure with better oxygen movement and higher conductivity. When the heating rate was increased, the maximum temperature of the second endothermic feature was shifted to the lower temperatures. This implies that the process of phase change has been activated. The activation energy for this endothermic process was estimated to be 81 kcal/mole based on the method of Ozawa.¹⁶

Conclusion

(1) Our results demonstrate that the NEXAFS technique is a very useful tool in investigating metal oxide catalysts. It can be applied to in situ catalytic reaction studies.

(2) The oxygen K-edge NEXAFS features can be used as 'fingerprints' for the identification of MoO_x species.

(3) The NEXAFS and DSC investigation shows that lattice oxygen migrates into the surface and reacts with CH_4 in the oxidation process over the $\text{MoO}_3/\text{SiO}_2$ catalyst.

Acknowledgment. This paper was supported in part by NON DIRECTED RESEARCH FUND, Korea Research Foundation and in part by the Korean Science and Engineering Foundation through the Science Research Center of Excellent Program (1995).

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Preparation of A New HPLC Chiral Stationary Phase from (S)-Naproxen and Application in Elucidating Chiral Recognition Models

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Received June 23, 1997

A new HPLC chiral stationary phase (CSP 3) has been prepared by connecting N-phenyl N-propyl amide of (S)-naproxen to silica gel through the 6-methoxy-2-naphthyl group of (S)-naproxen. The new CSP has been applied in resolving a homologous series of N-(3,5-dinitrobenzoyl)- α -amino acid esters and a homologous series of N-(3,5-dinitrobenzoyl)- α -(4-alkylphenyl)alkylamines. The separation factors, α , for resolving a homologous series of N-(3,5-dinitrobenzoyl)- α -amino esters and a homologous series of N-(3,5-dinitrobenzoyl)- α -(4-alkylphenyl)alkylamines on the new CSP have been found to remain almost constant throughout the wide range of the length of the alkyl substituent of the analytes while those on the previously reported CSPs (CSP 1 and 2) which were prepared by connecting N-phenyl N-propyl amide of (S)-naproxen to silica gel through the N-propyl group increase or decrease continuously. These results are concluded to support the chiral recognition models which utilize the intercalation of the alkyl substituent of the racemic analytes between the adjacent strands of CSP 1 or 2 to rationalize the increasing or decreasing trends of separation factors.

Introduction

Liquid chromatographic resolution of enantiomers on CSPs has been known to be one of the most convenient and accurate means in determining the enantiomeric composition of racemic compounds.¹ Consequently, various efforts have been devoted to the development of effective HPLC CSPs.² Among others, Pirkle-type CSPs have been known to resolve racemates through enantioselective π - π interaction between the CSP and racemic analytes.³ For the effective π - π interaction with racemic analytes, Pirkle-type CSPs have been usually designed to contain π -acidic and/or π -basic aromatic rings.⁴ In this context, (S)-naproxen, which is well known as an anti-inflammatory drug and readily available as an optically active form,⁵ is an attractive chiral selector of Pirkle-type CSPs because its 6-methoxy-2-naphthyl group can be utilized as an effective π -basic interaction site.

The use of (S)-naproxen as an effective chiral selector has indeed been demonstrated by various Pirkle-type CSPs.⁶ For example, CSP 1 prepared by connecting N-phenyl-N-(10-undecenyl) amide of (S)-naproxen to silica gel was suc-

cessfully used in resolving various π -acidic racemates and the enantioselectivities on it were found to be greater than those on any other (S)-naproxen-derived CSPs reported.^{6f} In order to elucidate the chiral recognition mechanism exerted by CSP 1, a CSP with a short connecting tether (CSP 2) was prepared and from the chiral resolution trends for resolving homologous series of π -acidic racemates on CSP 1 and CSP 2, chiral recognition models utilizing the intercalation of the alkyl substituent of the analyte between the adjacent strands of bonded phase were proposed.^{6h} However, the chiral recognition models proposed should be confirmed or modified by accumulating additional experimental evidences.

As an effort to provide additional experimental evidences for the chiral recognition models proposed for CSP 1 or 2, we prepared in this study another CSP (CSP 3) based on (S)-naproxen. CSP 3 has the same structure as that of CSP 1 or 2 except the connecting tether direction. Consequently, it is expected that the chromatographic resolution trends observed on CSP 3 should be different from those assumed to be resulted from the intercalation of the alkyl substituent of the racemic analytes between the adjacent strands of CSP 1 or 2.