# Spillover and Migration of Alkoxy Groups Formed by Adsorption of Alcohols on Silica-supported Molybdenum Oxide

M. Seman, J. N. Kondo, K. Domen, and S. T. Oyama†
*Chemical Resources Laboratory, Tokyo Institute of Technology, Nagatsuta 4259, Midori-ku, Yokohama, 226-8503*
*†Environmental Catalysis and Materials Laboratory, Department of Chemical Engineering, Virginia Tech,*
*Blacksburg, Virginia 24061, U. S. A.*

(Received August 2, 2002; CL-020644)

Alcohol adsorption on $MoO_3/SiO_2$ resulted in formation of two types of alkoxide, spectator and participant for selective oxidation, which exist on $SiO_2$ consuming silanol groups through spillover and migration from $MoO_3$ to $SiO_2$ support.

---

Alcohol adsorption on the supported metal oxide catalysts is known to form surface alkoxy groups.[1–5] It is commonly presumed that the alkoxy groups are located on the active metal,[6–10] while the support is not directly involved in the alkoxy formation. In this study, different roles of both the active metal and the support are proposed on the bases of experimental results using 1 wt% molybdenum oxide supported on silica catalyst ($MoO_3/SiO_2$).

1 wt% $MoO_3/SiO_2$ was prepared by the impregnation of an aqueous solution of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, Aldrich >99.99%) on silica (Cabosil EH-5, 350 $m^2g^{-1}$) using the incipient wetness technique, followed by drying at 120 °C for 6 h and calcination at 500 °C for 6 h.[11] Surface area was measured as 337 $m^2g^{-1}$, and oxygen chemisorption (uptake) amount at the point of initial reduction of the sample was 37 $\mu$mol $g^{-1}$,[11] corresponding to 0.074 mmol Mo $g^{-1}$. The metal dispersion is confirmed to be close to 100%.[11] The catalyst (a thin self-supporting wafer, 20 mg) was placed inside of a heatable IR cell with KBr windows. The gaseous mixture consisted of methanol and/or oxygen diluted in He and was fed at a total flow rate of 94 $cm^3$ (NTP) $min^{-1}$ (66 $\mu$mol $s^{-1}$). The FTIR spectra were recorded at a resolution 4 $cm^{-1}$ by a spectrometer (Jasco, model 620) equipped with a TGS (triglycine sulfate) detector, with the measurements from 32 scans usually averaged. The outlet of the IR cell is connected through a 10-ways valve to a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID).

After pretreating the $MoO_3/SiO_2$ catalyst at 350 °C in He/$O_2$ for 5 h, the isolated Si-OH band at 3740 $cm^{-1}$ became very sharp and intense. The spectra a) and c) in Figure 1 show adsorption of $CH_3OH$ and $CD_3OD$, respectively, on $MoO_3/SiO_2$ at ca. 40 °C. The spectra b) and d) show adsorption of $CH_3OH$ and $CD_3OD$, respectively, at 250 °C. In Figure 1a) the C-H vibrations at 2999, 2957, and 2857 $cm^{-1}$ characterized methoxy groups formed from methanol adsorption. As the methoxy bands appeared and increased in intensity, the 3740 $cm^{-1}$ band of Si-OH was consumed, which is observed as a negative band. The formation rate of methoxide is initially rapid, but as the surface was reaching the saturation amount it slowed down.

The surface of $MoO_3/SiO_2$ became fully saturated by methoxide species within 40 min as noticed by a complete consumption of silanol groups, while the surface silanol groups of bare $SiO_2$ are only occupied to an extent of 58% of the maximum amount even after 14 h. Therefore, the adsorption process is markedly promoted by molybdenum oxide. The adsorption of deuterated methanol results in the formation of deuterated methoxy groups ($CD_3O$), characterized by C-D bands at 2240, 2141 and 2080 $cm^{-1}$. In the spectrum measured at 40 °C (Figure 1c)), physisorbed $CD_3OD$ has a very broad OD band at around 2500 $cm^{-1}$, while the broad band of physisorbed $CH_3OH$ at around 3350 $cm^{-1}$ is absent, indicating that the broad OH band observed in Figure 1a) belongs to $CH_3OH$ and not to the hydrogen bonded silanol groups. Therefore, silanol groups are found to disappear rather than to form a hydrogen bond to methanol. This confirms the quick water formation followed by immediate desorption of water and methoxide formation on $SiO_2$.

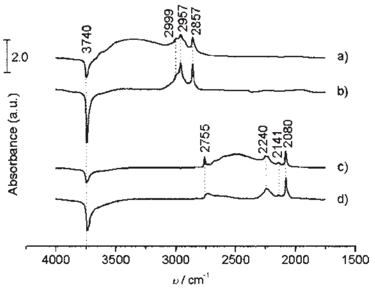

**Figure 1.** a) $CH_3OH$ adsorbed on $MoO_3/SiO_2$ at ca. 40 °C; b) $CH_3OH$ adsorbed on $MoO_3/SiO_2$ at 250 °C; c) $CD_3OD$ adsorbed on $MoO_3/SiO_2$ at ca. 40 °C; d) $CD_3OD$ adsorbed on $MoO_3/SiO_2$ at 250 °C. Spectra are measured after 60 min and shown after subtraction of a spectrum before absorption (pretreated sample).

A quantitative comparison of the number of surface alkoxy groups to the number of OH groups and molybdenum atoms is possible by the knowledge of the extinction coefficient of the Lambert-Beer's Law. The extinction coefficient is the slope of the integrated IR intensity versus adsorbed molar amount curve, assuming that 1 alcohol molecule produces 1 alkoxy group. Small amounts of methanol (0.57–5.8 mol%) diluted in He were in successive steps quantitatively adsorbed on the catalyst at 250 °C and the IR intensity of the 2857 $cm^{-1}$ band was recorded after each step. At the saturation point the intensity of the 3740 $cm^{-1}$ band of silanol decreased almost to zero, as mentioned above, indicating nearly complete replacement by methoxy groups. Therefore, it was possible to estimate the number of OH groups by comparing the intensities of the 2857 $cm^{-1}$ (methoxy) band and the 3740 $cm^{-1}$ (OH) band using a close gas-circulation system. The amount of surface methoxy groups at the saturation point was estimated 0.39 mmol $g^{-1}$, while the amount of OH groups on the pretreated sample 0.41 mmol $g^{-1}$. Recalling the quantity of surface Mo atoms (0.074 mmol Mo $g^{-1}$), at the saturation point the ratio of methoxy groups to molybdenum atoms is 5.6, which clearly indicates that the methoxy groups must be mainly located on the silica support as Si-$OCH_3$. Evidently, the methoxy groups are first formed on the molybdenum site and then undergo spillover onto the silica support. This process is further confirmed by the observations during the oxidation reaction.

The quantitation of the deuterated methoxide species is similarly carried out using its 2080 $cm^{-1}$ band. In He/$O_2$ flow, the methoxy groups were oxidized and decreased, and the silanol groups recovered at the same time. In the case of deuterated methoxy groups, an intense band at 2755 $cm^{-1}$ characterized the formation of Si-OD groups. The selective reaction intermediates to the final formaldehyde products are observable by C=O stretching at 1776 and 1750 $cm^{-1}$ in the case of $CH_3O$ oxidation and 1708, 1754 $cm^{-1}$ in the case of $CD_3O$ oxidation. The intermediates are most probably formyl groups. The oxidation rate was initially rapid, but after a certain time it slowed down, while a certain quantity of the alkoxy groups remained intact on the surface. The rapidly oxidized methoxides and slowly oxidized methoxides are obviously two different types of alkoxy groups, highly reactive species (participants) and slowly reacting spectators (Figure 2). The spectator species probably reside in a limited number of sites, featured by particular stability. The rapidly reacting species are formed on the Mo center, then spill over to the silica surface, but can migrate back to the Mo to be oxidized.

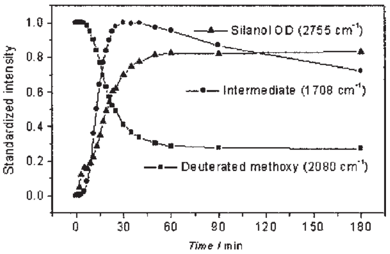

**Figure 2.** Time course of oxidation: Amounts of silanol OD groups, deuterated methoxy groups and intermediate species at 250 °C.

The ratio of the amount of quickly disappearing species and slowly disappearing species is 4.5 and 1.1 species, respectively, per 1 molybdenum oxide at 250 °C. Stability of the active and spectator species during adsorption was examined by sequential adsorption of deuterium-labeled and unlabeled methanol. Deuterated methanol ($CD_3OD$) was adsorbed on freshly pretreated $MoO_3/SiO_2$ to form $CD_3O$ species. After reaching the saturation point, the feed was switched to unlabeled $CH_3OH$ and the formation of $CH_3O$ species was observed (Figure 3). The $CH_3O$ formation in this manner is analogous to the formation over fresh surface: in the beginning rapid and slows down with increasing saturation. After 180 min, there is still substantial amount of $CD_3O$ groups, which are not exchanged, quantitatively corresponding to the spectator species as mentioned above. As a result, it is concluded that all active methoxy groups are exchangable, while the spectator species remain unperturbed.

To confirm migration of the methoxide species on the $MoO_3$/$SiO_2$ surface, simultaneous oxidation of $CH_3O$ and $CD_3O$ species was conducted. The surface was saturated with $CH_3O$ species, and approximately half of the amount was replaced by $CD_3O$ species. However, when the catalyst was exposed to oxygen, both $CH_3O$ and $CD_3O$ species started to be oxidized at the same time by rates almost precisely identical as for the individual oxidation, which indicates that the active methoxides have mobility to be mixed. When the oxidation rate nearly stopped, the surface was covered by a homogeneous mixture of remaining $CH_3O$ and $CD_3O$ species in amount, which corresponds to the spectator species as mentioned above.

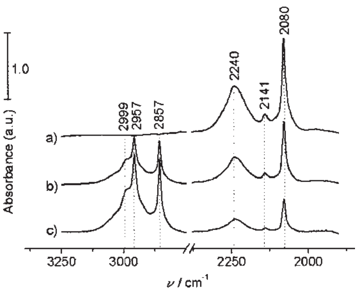

**Figure 3.** Spectra during methanol isotopic exchange on $MoO_3/SiO_2$: a) surface with $CD_3O$ groups; b), c) $CD_3O$ groups partially exchanged by $CH_3O$ groups (20 and 180 min, respectively, after the methanol switch).

From the sequential adsorption of deuterium-labeled and unlabeled methanol experiment, it would be expected that the inactive spectator species do not migrate. However, in the simultaneous oxidation experiment it was found that the spectator species became a homogeneous mixture of $CH_3O$ and $CD_3O$ species. The difference lies in the fact that the adsorption sites of methoxy groups were always saturated in the exchange experiment, so the mobility of methoxide species was limited, and restricted to the reactive species. In the oxidation experiment, the coverage of methoxides gradually decreased, which increased the mobility of the two types of methoxide.

Methoxy formation from methanol adsorption is a well-known reaction, which has been reported by many authors. The original finding of this study is the fact that alkoxy groups are first formed on Mo and then spillover to the $SiO_2$ surface, consuming silanol groups. The stoichiometry of alkoxy groups, Mo atoms and silanol groups confirmed the spillover and migration of alkoxy groups. Furthemore, almost 100% of silanol groups were found to be occupied by the alkoxy groups. Therefore, the dynamic equilibrium of surface alkoxy groups during the reaction is clarified.

## References

1 L. E. Briand, W. E. Farneth, and I. E. Wachs, *Catal. Today*, **62**, 219 (2000).
2 L. J. Burcham and I. E. Wachs, *Catal. Today*, **49**, 467 (1999).
3 M. A. Natal-Santiago and J. A. Dumesic, *J. Catal.*, **175**, 252 (1998).
4 M. Mavrikakis and M. A. Barteau, *J. Mol. Catal. A: Chem*, **131**, 135 (1998).
5 J. E. Sambeth, M. A. Centeno, A. Paúl, L. E. Briand, H. J. Thomas, and J. A. Odriozola, *J. Mol. Catal. A: Chem*, **161**, 89 (2000).
6 H. Hu, I. E. Wachs, and S. R. Bare, *J. Phys. Chem.*, **99**, 10897 (1995).
7 G. Deo, I. E. Wachs, and J. Haber, *Crit. Rev. Surf. Chem.*, **40**, 1 (1994).
8 J. M. Jehng and I. E. Wachs, *Catal. Today*, **16**, 417 (1993).
9 M. A. Vuurman, D. J. Stufkens, A. Oskam, and I. E. Wachs, *J. Mol. Catal.*, **76**, 263 (1992).
10 M. A. Vuurman, I. E. Wachs, D. J. Stufkens, and A. Oskam, *J. Mol. Catal.*, **80**, 209 (1993).
11 R. Radhakrishnan, C. Reed, S. T. Oyama, M. Seman, J. N. Kondo, K. Domen, Y. Ohminami, and K. Asakura, *J. Phys. Chem. B*, **105**, 8519 (2001).