The new catalytic property of supported rhenium oxides for selective oxidation of methanol to methylal

Youzhu Yuan, Takafumi Shido and Yasuhiro Iwasawa*

Department of Chemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan. E-mail: iwasawa@chem.s.u-tokyo.ac.jp

Received (in Cambridge, UK) 15th May 2000, Accepted 23rd June 2000

A new catalytic property of supported rhenium oxides has been found for selective methanol oxidation to methylal; high performances for the selective catalytic oxidation are observed with V_2O_5-, ZrO_2-, Fe_2O_3- and TiO_2-supported Re–oxide catalysts, which are characterized by pulse experiments, XRD and XPS.

Numerous efforts have been made to develop selective oxidation catalysts for methanol conversions to formaldehyde, methyl formate and dimethoxymethane (methylal). Methanol oxidation to formaldehyde has been extensively studied and commercialized on silver and ferric molybdate catalysts.[1] High-yield production of methyl formate from methanol has also been accomplished on mixed metal oxides such as V–Ti oxides,[2] Sn–Mo oxides,[3] and Bi-based oxides.[4] Methylal is used as a gasoline additive, a solvent in perfume industry, a key intermediate for preparing high concentration formaldehyde, and a reagent in organic synthesis. The catalytic methylal synthesis from methanol ($3\ MeOH + 1/2\ O_2 \rightarrow CH_2(OMe)_2 + 2\ H_2O$) has been reported on V/TiO_2,[1] V–Mo–O,[5] PMoH–5.75/SiO_2,[6,7] Mo/MCM-41,[8] and MoO_3(100),[9,10] but the selectivities to methylal on those catalysts were low. Recently, we found a crystalline binary oxide compound SbR_2O_6 which was selective for the methylal formation.[11] The selectivity reached 93.5% at a conversion of 6.5% at 573 K. However, the crystalline oxide $SbRe_2O_6$ has a very low surface area (1 $m^2\ g^{-1}$), resulting in insufficient activity for methylal production. The performance of SbR_2O_6 was attributed to the Re–oxide octahedra connecting with Sb–O chains.[11] The property of Re species capable of adopting a variety of oxidation states that are illustrated in both binary and ternary oxides,[12–14] may provide rich and interesting chemistry. Nevertheless, Re oxides have not widely been used as catalysts for selective oxidation reactions owing to sublimation under pretreatment and reaction conditions.[15] In this study we have found the new catalytic property of supported and unsupported Re oxides for the selective methanol oxidation to methylal.

Inorganic oxide-supported Re oxide catalysts were prepared by an incipient wetness impregnation method using an aqueous solution of ammonium perrhenate (NH_4ReO_4), followed by drying at 383 K for 12 h. The samples were put into a glass-made fixed-bed reactor in a flow system and heated to 673 K at a heating rate of 4 K min^{-1} in a He flow and held at 673 K for 6 h. The samples thus obtained were further treated *in situ* in the fixed-bed flow reactor under the He flow at 573 K for 1 h before use as catalysts. A typical Re loading was 10 wt% as Re/support. Methanol (Wako, purity 99.8%) was introduced to the flow reactor by bubbling He gas through a glass saturator filled with methanol. Unsupported Re oxides were also pretreated at 673 K in a similar way. The catalytic reactions on the supported and unsupported Re–oxide catalysts were carried out at 513 K under the reaction conditions GHSV = 40 000 ml $h^{-1}\ g_{cat}^{-1}$ and $He:O_2:MeOH$ = 86.3:9.7:4.0 (mol%) at 1 atm. The products were analyzed by an on-line gas chromatograph using Porapak N and Unibeads C columns.

Table 1 shows the performances of the supported Re–oxide catalysts for the selective methanol oxidation to methylal. The performances of unsupported Re oxides (ReO_3 and ReO_2) and two typical supports (α-Fe_2O_3 and V_2O_5) are also listed in Table 1 for comparison.

It was found that Re oxides supported on TiO_2 (rutile and anatase), V_2O_5, ZrO_2 (monoclinic), Fe_2O_3 (α and γ) and α-Al_2O_3 were active in order of the reaction rates per g_{Re} for the supports, TiO_2(anatase) > TiO_2(rutile) > γ-Fe_2O_3 > ZrO_2 > V_2O_5 > α-Fe_2O_3. Among them, Re/V_2O_5, Re/γ-Fe_2O_3, Re/α-Fe_2O_3, Re/ZrO_2 and Re/α-Al_2O_3 showed selectivities of 88–94% to methylal (Table 1). When the conversion for Re/γ-Fe_2O_3 was further increased by decreasing the space velocity, the methylal selectivity decreased a little, while the formaldehyde selectivity increased. Re oxides supported on SiO_2

Table 1 Catalytic methanol oxidation on supported Re–oxide catalysts at 513 K[a]

Catalyst	$S_{BET}/m^2\ g^{-1}$	MeOH conversion mol%	MeOH conversion Rate/mmol $h^{-1}\ g^{-1}$	Selectivity (mol%) $CH_2(OMe)_2$	HCHO	Me_2O	HCO_2Me	CO_x[b]
Re/TiO_2-rutile	5	53.7	351.2	83.1	1.9	0.7	9.1	5.2
Re/TiO_2-anatase	50	59.5	389.1	78.5	4.1	1.1	11.7	4.6
Re/V_2O_5	6	21.5	140.6	93.7	0.0	4.3	0.0	2.0
Re/ZrO_2	9	35.8	234.1	89.4	2.0	Trace	7.6	1.0
Re/α-Fe_2O_3	3	15.5	101.4	90.5	2.0	1.0	6.0	0.5
Re/γ-Fe_2O_3	16	48.4	319.2	91.0	2.4	1.0	4.6	1.0
Re/SiO_2	36	15.1	98.8	60.7	1.3	Trace	11.9	26.1
Re/α-Al_2O_3	10	16.3	106.6	88.3	2.8	Trace	5.9	2.9
Re/Sb_2O_3	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Re/Bi_2O_3	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Re/MoO_3	5	9.1	59.5	80.0	0.0	19.0	0.0	1.0
α-Fe_2O_3	3	0.0	0.0	0.0	0.0	0.0	0.0	0.0
V_2O_5	6	9.3	10.8[c]	1.0	91.5	7.4	0.0	Trace
ReO_3	1	12.4	10.2	99.0	0.0	0.5	0.5	0.0
ReO_2	7	65.3	50.0	64.6	6.4	2.0	10.2	16.8

[a] Re loading: 10.0 wt%, GHSV = 40 000 ml $h^{-1}\cdot g_{cat}$, $He:O_2:MeOH$ = 86.3:9.7:7:4 (mol%). [b] CO_x = CO_2 + CO. [c] mmol $h^{-1}\ g_V^{-1}$.

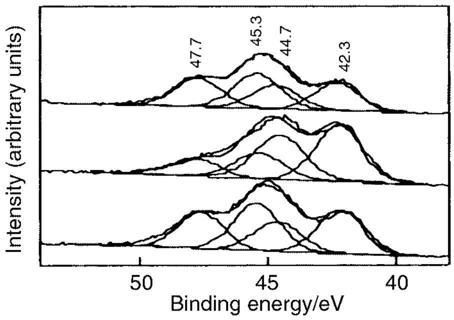

Fig. 1 Re 4f XPS spectra for 10.0 wt% Re/α-Fe_2O_3 catalysts: (a) after pretreatment at 673 K for 6 h in He, (b) after ten methanol pulses at 513 K and (c) after catalytic methanol oxidation at 513 K for 2 h in the presence of O_2. The XPS binding energies were referred to 284.6 eV for C 1s.

produced a significant amount of CO_x and those supported on Sb_2O_3 and Bi_2O_3 showed no activity at 513 K (Table 1). α-Fe_2O_3 and V_2O_5 themselves were almost inactive for methylal formation though V_2O_5 produced formaldehyde. When these oxides were supported by Re oxides, the obtained Re/α-Fe_2O_3 and Re/V_2O_5 showed selectivities to methylal as high as 91–94%. ReO_3 was most selective (99%), while the selectivity of ReO_2 was much lower (64.6%). When the mixture of He–MeOH–O_2 was admitted to Re_2O_7 at 513 K, the color changed from yellow (Re_2O_7) to read (ReO_3) in < 3 min, accompanied with sublimation of some of the Re_2O_7, and showed a selectivity to methylal > 90% after 10 min of time-on-stream. Under the reaction conditions below 553 K, there was no loss of Re oxides by sublimation in Re/TiO_2, Re/V_2O_5, Re/Fe_2O_3, Re/ZrO_2, Re/SiO_2, Re/Al_2O_3 and Re/MoO_3. It indicates that bulk Re_2O_7 is not a stable phase in the methylal synthesis conditions. It was concluded from plots of the selectivities against the reaction rates per surface area or the conversions in Table 1 that Re/α-Fe_2O_3, Re/γ-Fe_2O_3, Re/V_2O_5 and Re/ZrO_2 exhibit high catalytic selectivity on Re/α-Fe_2O_3 increased with increasing Re loading and reached saturation values at 2.0 wt% Re (15.5 and 92.0%, respectively). The highest reaction rates per g_{Re} of the supported Re–oxide catalysts were thus achieved in the range of Re loadings 1–3 wt%.

Recently, a high selectivity of 76.2% was reported on 2 mol% Mo supported on MCM-41, but it was achieved at a very low conversion of 0.7% at 543 K.[8] Further, the Mo/MCM-41 catalyst was rapidly deactivated owing to a significant leaching of Mo species from the channels of MCM-41.[8] On the other hand, no deactivation of the supported Re oxides occurred for 6 h of time-on-stream at 513 K. Methylal formation from methanol was also reported on PMoH–5.75/SiO_2[6,7] and V/TiO_2,[1] but the selectivities toard methylal were as low as 40–56%.[11]

The XPS spectrum [Fig. 1(a)] for the as-pretreated Re/α-Fe_2O_3 showed a peak at 42.3 eV which is assigned to the Re $4f_{7/2}$ level for Re^{4+} species (also deconvoluted at 44.7 eV for $4f_{5/2}$). The XPS spectrum also showed peaks at 45.3 and 47.7 eV assigned to Re $4f_{7/2}$ and $4f_{5/2}$ levels possibly for a Re^{6+} species, respectively [Fig. 1(a)]. The Re $4f_{7/2}$ binding energy (45.3 eV) is lower by 1.2–1.6 eV than that reported for Re_2O_7 (R^{7+}), but higher by 0.8–1.0 eV than that for ReO, (Re^{6+}).[17,18] We measured XPS spectra for the Re/α-Fe_2O_3 catalysts with different Re loadings in the range 0.1–10.0 wt%. The Re^{6+} peaks at 45.3 and 47.7 eV were observed in all the samples, while the Re^{4+} peaks at 42.3 and 44.7 eV developed only for the catalysts with Re $>$ 2.0 wt%. The XRD lines for ReO_2 appeared for the Re/α-Fe_2O_3 catalysts with Re $>$ 3.0 wt%, while no diffraction lines due to Re_2O_7 and ReO_3 were detected. It is most likely from these results that the initial Re^{7+} precursors were reduced to Re^{6+} and also to Re^{4+} for Re loadings above 2.0 wt% under the pretreatment conditions.[16] We estimate 2 wt% of Re as a monolayer of Re oxides at the α-Fe_2O_3 surface. The fact that neither Re^{4+} (XPS) nor ReO_2 (XRD) were detected on the catalysts with Re loadings below 2.0 wt% indicates that dispersed Re oxides are scarcely reduced to Re^{4+} under He at 673 K probably because of interaction with the α-Fe_2O_3 surface.

When pulses of 1 ml of He–MeOH = 96.0 : 4.0 (mol%) were introduced onto the 10.0 wt% Re/α-Fe_2O_3 catalyst at 513 K, methylal was formed during the course of the first to fourth methanol pulses with decreasing selectivities, and after the fifth pulse no methylal was produced. It is evident from the pulse experiments in the absence of gaseous O_2 that lattice oxygen atoms of the Re oxides work as active oxygen species for the selective oxidation of methnol. From the pulse experiments where the 10 wt% Re/α-Fe_2O_3 catalyst reacted with the methanol pulses at 513 K, we estimated that the amount of lattice oxygen atoms incorporated into the produced methylal was 1.88×10^{19} atom m^{-2}. Exhaustion of the active oxygen atoms increased the formation of H_2, CH_4 and CO_2 in a molar ratio of nearly 2 : 1 : 1 probably through decomposition of HCO_2Me produced preferable on the reduced Re oxides. After ten methanol pulses at 513 K, the intensities of the XPS peaks at 45.3 and 47.7 eV assigned to Re^{6+} species decreased drastically, while the Re^{4+} peak intensities increased significantly [Fig. 1(b)]. The consumed lattice oxygen atoms were regenerated by gaseous O_2 as established by XPS spectroscopy [Fig. 1(c)].

In summary, we have developed supported Re–oxide catalysts which show high performances for selective catalytic oxidation of methanol to methylal. The high performances of the Re oxides were obtained when V_2O_5, ZrO_2 and Fe_2O_3 were used as supports. The redox capability of Re oxides at the support surfaces (possibly $Re^{6+} \leftrightarrows Re^{4+}$) may be responsible for the selective oxidation of methanol to formaldehyde, while the appropriate acidy Re oxides may also be necessary for the acetalization of formaldehyde with methanol to form methylal.

This work was supported by Core Research for Evolutional Science and Technology (CREST) of Japan Science and Technology Corporation (JST).

Notes and references

1 J. M. Tatibouët, *Appl. Catal. A: Gen.*, 1997, **148**, 213.
2 G. Busca, A. S. Elmi and P. Forzatti, *J. Phys. Chem.*, 1987, **91**, 5236.
3 M. Ai, *J. Catal.*, 1982, **77**, 279.
4 N. Arora, G. Deo, I. E. Wachs and A. M. Hirt, *J. Catal.*, 1996, **159**, 1.
5 J. M. Tatibouët and J. E. Germain, *Bull. Soc. Chem. Fr. I*, 1980, **9–10**, 343.
6 M. Fournier, A. Aouissi and C. Rocchiccioli-Deltchff, *J. Chem. Soc., Chem. Commun.*, 1994, 307.
7 C. Rocchiccioli-Deltcheff, A. Aoussi, S. Launary and M. Fournier, *J. Mol. Catal. A: Chem.*, 1996, **114**, 331.
8 I. J. Shannon, T. Maschmeyer, R. D. Oldroyd, G. Sankar, J. M. Thomas, H. Pernot, J. P. Baalikdjian and M. Che, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 1495.
9 J. M. Tatibouët and J. E. Germain, *J. Catal.*, 1981, **72**, 375.
10 J. M. Tatibouët, J. E. Germain and J. C. Volta, *J. Catal.*, 1983, **32**, 240.
11 Y. Yuan, H. Liu, H. Imoto, T. Shido and Y. Iwasawa, *Chem. Lett.*, 2000, 674.
12 H. Liu, E. C. Gaigneaux, H. Imoto, T. Shido and Y. Iwasawa, *J. Phys. Chem.*, 2000, **104**, 2033.
13 H. Watanebe, H. Imoto and H. Tanaka, *J. Solid State Chem.*, 1998, **138**, 245.
14 A. Butz, G. Miehe, H. Paulus, P. Strauss and H. Fuess, *J. Solid State Chem.*, 1998, **138**, 232.
15 S. Albonetti, F. Cavani and F. Trifiro, *Catal. Rev.-Sci. Eng.*, 1996, **38**, 413.
16 Y. Yuan, T. Shido and Y. Iwasawa, to be published.
17 E. S. Shpiro, V. I. Avaev, G. V. Antoshin, M. A. Ryashentseva and K. M. Minachev, *J. Catal.*, 1978, **44**, 402.
18 A. Cimino, B. A. De Angelis, D. Gazzoli and M. Valigi, *Z. Anorg. Allg. Chem.*, 1980, **460**, 86.