

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

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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.<sup>1</sup> High-yield production of methyl formate from methanol has also been accomplished on mixed metal oxides such as V–Ti oxides,<sup>2</sup> Sn–Mo oxides,<sup>3</sup> and Bi-based oxides.<sup>4</sup> 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 ( $3\text{ MeOH} + 1/2\text{ O}_2 \rightarrow \text{CH}_2(\text{OMe})_2 + 2\text{ H}_2\text{O}$ ) has been reported on V/TiO<sub>2</sub>,<sup>1</sup> V–Mo–O,<sup>5</sup> PMoH–5.75/SiO<sub>2</sub>,<sup>6,7</sup> Mo/MCM-41,<sup>8</sup> and MoO<sub>3</sub>(100),<sup>9,10</sup> but the selectivities to methylal on those catalysts were low. Recently, we found a crystalline binary oxide compound SbR<sub>2</sub>O<sub>6</sub> which was selective for the methylal formation.<sup>11</sup> The selectivity reached 93.5% at a conversion of 6.5% at 573 K. However, the crystalline oxide SbRe<sub>2</sub>O<sub>6</sub> has a very low surface area (1 m<sup>2</sup> g<sup>−1</sup>), resulting in insufficient activity for methylal production. The performance of SbR<sub>2</sub>O<sub>6</sub> was attributed to the Re-oxide octahedra connecting with Sb–O chains.<sup>11</sup> The property of Re species capable of adopting a variety of oxidation states that are illustrated in both binary and ternary oxides,<sup>12–14</sup> 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.<sup>15</sup> 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<sub>4</sub>ReO<sub>4</sub>), 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<sup>−1</sup> 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<sup>−1</sup> g<sub>cat</sub><sup>−1</sup> and He:O<sub>2</sub>: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.

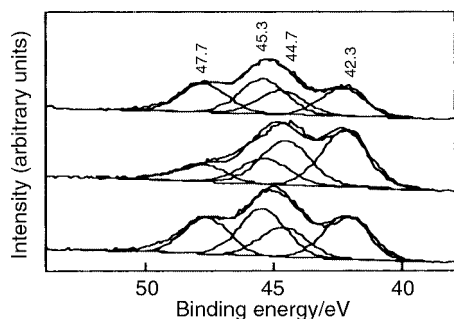
Table 1 shows the performances of the supported Re-oxide catalysts for the selective methanol oxidation to methylal. The performances of unsupported Re oxides (ReO<sub>3</sub> and ReO<sub>2</sub>) and two typical supports ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub>) are also listed in Table 1 for comparison.

It was found that Re oxides supported on TiO<sub>2</sub> (rutile and anatase), V<sub>2</sub>O<sub>5</sub>, ZrO<sub>2</sub> (monoclinic), Fe<sub>2</sub>O<sub>3</sub> ( $\alpha$  and  $\gamma$ ) and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> were active in order of the reaction rates per g<sub>Re</sub> for the supports, TiO<sub>2</sub>(anatase) > TiO<sub>2</sub>(rutile) >  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> > ZrO<sub>2</sub> > V<sub>2</sub>O<sub>5</sub> >  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Among them, Re/V<sub>2</sub>O<sub>5</sub>, Re/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, Re/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, Re/ZrO<sub>2</sub> and Re/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> showed selectivities of 88–94% to methylal (Table 1). When the conversion for Re/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> was further increased by decreasing the space velocity, the methylal selectivity decreased a little, while the formaldehyde selectivity increased. Re oxides supported on SiO<sub>2</sub>

Table 1 Catalytic methanol oxidation on supported Re-oxide catalysts at 513 K<sup>a</sup>

Catalyst	$S_{\text{BET}}/\text{m}^2\text{ g}^{-1}$	MeOH conversion		Selectivity (mol%)				
		mol%	Rate/mmol h <sup>−1</sup> g <sup>−1</sup>	CH <sub>2</sub> (OMe) <sub>2</sub>	HCHO	Me <sub>2</sub> O	HCO <sub>2</sub> Me	CO <sub>x</sub> <sup>b</sup>
Re/TiO <sub>2</sub> -rutile	5	53.7	351.2	83.1	1.9	0.7	9.1	5.2
Re/TiO <sub>2</sub> -anatase	50	59.5	389.1	78.5	4.1	1.1	11.7	4.6
Re/V <sub>2</sub> O <sub>5</sub>	6	21.5	140.6	93.7	0.0	4.3	0.0	2.0
Re/ZrO <sub>2</sub>	9	35.8	234.1	89.4	2.0	Trace	7.6	1.0
Re/ $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	3	15.5	101.4	90.5	2.0	1.0	6.0	0.5
Re/ $\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	16	48.4	319.2	91.0	2.4	1.0	4.6	1.0
Re/SiO <sub>2</sub>	36	15.1	98.8	60.7	1.3	Trace	11.9	26.1
Re/ $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	10	16.3	106.6	88.3	2.8	Trace	5.9	2.9
Re/Sb <sub>2</sub> O <sub>3</sub>	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Re/Bi <sub>2</sub> O <sub>3</sub>	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Re/MoO <sub>3</sub>	5	9.1	59.5	80.0	0.0	19.0	0.0	1.0
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	3	0.0	0.0	0.0	0.0	0.0	0.0	0.0
V <sub>2</sub> O <sub>5</sub>	6	9.3	10.8 <sup>c</sup>	1.0	91.5	7.4	0.0	Trace
ReO <sub>3</sub>	1	12.4	10.2	99.0	0.0	0.5	0.5	0.0
ReO <sub>2</sub>	7	65.3	50.0	64.6	6.4	2.0	10.2	16.8

<sup>a</sup> Re loading: 10.0 wt%, GHSV = 40 000 ml h<sup>−1</sup> g<sub>cat</sub><sup>−1</sup>, He:O<sub>2</sub>:MeOH = 86.3:9.7:7.4 (mol%). <sup>b</sup> CO<sub>x</sub> = CO<sub>2</sub> + CO. <sup>c</sup> mmol h<sup>−1</sup> g<sub>v</sub><sup>−1</sup>.



**Fig. 1** Re 4f XPS spectra for 10.0 wt% Re/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>. The XPS binding energies were referred to 284.6 eV for C 1s.

produced a significant amount of CO<sub>x</sub> and those supported on Sb<sub>2</sub>O<sub>3</sub> and Bi<sub>2</sub>O<sub>3</sub> showed no activity at 513 K (Table 1).  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> themselves were almost inactive for methylal formation though V<sub>2</sub>O<sub>5</sub> produced formaldehyde. When these oxides were supported by Re oxides, the obtained Re/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Re/V<sub>2</sub>O<sub>5</sub> showed selectivities to methylal as high as 91–94%. ReO<sub>3</sub> was most selective (99%), while the selectivity of ReO<sub>2</sub> was much lower (64.6%). When the mixture of He–MeOH–O<sub>2</sub> was admitted to Re<sub>2</sub>O<sub>7</sub> at 513 K, the color changed from yellow (Re<sub>2</sub>O<sub>7</sub>) to red (ReO<sub>3</sub>) in <3 min, accompanied with sublimation of some of the Re<sub>2</sub>O<sub>7</sub>, 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<sub>2</sub>, Re/V<sub>2</sub>O<sub>5</sub>, Re/Fe<sub>2</sub>O<sub>3</sub>, Re/ZrO<sub>2</sub>, Re/SiO<sub>2</sub>, Re/Al<sub>2</sub>O<sub>3</sub> and Re/MoO<sub>3</sub>. It indicates that bulk Re<sub>2</sub>O<sub>7</sub> 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/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, Re/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, Re/V<sub>2</sub>O<sub>5</sub> and Re/ZrO<sub>2</sub> exhibit high catalytic selectivity on Re/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> 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<sub>Re</sub> 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.<sup>8</sup> Further, the Mo/MCM-41 catalyst was rapidly deactivated owing to a significant leaching of Mo species from the channels of MCM-41.<sup>8</sup> 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<sub>2</sub><sup>6,7</sup> and V/TiO<sub>2</sub>,<sup>1</sup> but the selectivities toward methylal were as low as 40–56%.<sup>11</sup>

The XPS spectrum [Fig. 1(a)] for the as-pretreated Re/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> showed a peak at 42.3 eV which is assigned to the Re 4f<sub>7/2</sub> level for Re<sup>4+</sup> species (also deconvoluted at 44.7 eV for 4f<sub>5/2</sub>). The XPS spectrum also showed peaks at 45.3 and 47.7 eV assigned to Re 4f<sub>7/2</sub> and 4f<sub>5/2</sub> levels possibly for a Re<sup>6+</sup> species, respectively [Fig. 1(a)]. The Re 4f<sub>7/2</sub> binding energy (45.3 eV) is lower by 1.2–1.6 eV than that reported for Re<sub>2</sub>O<sub>7</sub> (Re<sup>7+</sup>), but higher by 0.8–1.0 eV than that for ReO, (Re<sup>6+</sup>).<sup>17,18</sup> We measured XPS spectra for the Re/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> catalysts with different Re loadings in the range 0.1–10.0 wt%. The Re<sup>6+</sup> peaks at 45.3 and 47.7 eV were observed in all the samples, while the Re<sup>4+</sup> peaks at 42.3 and 44.7 eV developed only for the catalysts with Re > 2.0 wt%. The XRD lines for ReO<sub>2</sub> appeared for the Re/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> catalysts with Re > 3.0 wt%, while no diffraction lines due to Re<sub>2</sub>O<sub>7</sub> and ReO<sub>3</sub> were detected. It is most likely from these results that the initial Re<sup>7+</sup> precursors were reduced to Re<sup>6+</sup> and also to Re<sup>4+</sup> for Re loadings above 2.0 wt% under the pretreatment conditions.<sup>16</sup> We estimate 2 wt% of Re as a monolayer of Re oxides at the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> surface. The fact

that neither Re<sup>4+</sup> (XPS) nor ReO<sub>2</sub> (XRD) were detected on the catalysts with Re loadings below 2.0 wt% indicates that dispersed Re oxides are scarcely reduced to Re<sup>4+</sup> under He at 673 K probably because of interaction with the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> surface.

When pulses of 1 ml of He–MeOH = 96.0:4.0 (mol%) were introduced onto the 10.0 wt% Re/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> 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<sub>2</sub> that lattice oxygen atoms of the Re oxides work as active oxygen species for the selective oxidation of methanol. From the pulse experiments where the 10 wt% Re/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> catalyst reacted with the methanol pulses at 513 K, we estimated that the amount of lattice oxygen atoms incorporated into the produced methylal was  $1.88 \times 10^{19}$  atom m<sup>−2</sup>. Exhaustion of the active oxygen atoms increased the formation of H<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub> in a molar ratio of nearly 2:1:1 probably through decomposition of HCO<sub>2</sub>Me 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<sup>6+</sup> species decreased drastically, while the Re<sup>4+</sup> peak intensities increased significantly [Fig. 1(b)]. The consumed lattice oxygen atoms were regenerated by gaseous O<sub>2</sub> 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<sub>2</sub>O<sub>5</sub>, ZrO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> were used as supports. The redox capability of Re oxides at the support surfaces (possibly Re<sup>6+</sup>  $\rightleftharpoons$  Re<sup>4+</sup>) may be responsible for the selective oxidation of methanol to formaldehyde, while the appropriate acidic Re oxides may also be necessary for the acetalization of formaldehyde with methanol to form methylal.

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