

Selective Synthesis of Methylal from Methanol on a New Crystalline SbRe_2O_6 Catalyst

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A novel SbRe_2O_6 catalyst was active for the selective methanol oxidation to methylal ($\text{CH}_2(\text{OCH}_3)_2$). Other known Sb-Re oxides, $\text{Sb}_4\text{Re}_2\text{O}_{13}$ and $\text{SbOReO}_4 \cdot 2\text{H}_2\text{O}$ produced almost no methylal. The bulk and surface of the SbRe_2O_6 catalyst was characterized by XRD, Raman, XPS and SEM. The high performance of SbRe_2O_6 may be attributed to the Re-oxide octahedra connecting with Sb-O chains.

Numerous efforts have been made with development of selective oxidation catalysts for methanol conversion to oxygenates such as formaldehyde, methyl formate and dimethoxymethane (methylal) from both industrial and academic points of view. The oxidation of methanol to formaldehyde has been extensively studied and commercialized on silver and ferric molybdate catalysts.¹ It has also been demonstrated that methyl formate can be produced with high yields by the catalytic oxidation of methanol on V-Ti oxides,² Sn-Mo oxides³ and Bi-based mixed oxides.⁴ However, methylal, which is used as a gasoline additive, a solvent in perfume industry, and key intermediates for preparing high concentration formaldehyde and also in organic synthesis, has not successfully been produced by the catalytic oxidation of methanol. The catalytic methylal synthesis from methanol has been reported on V/TiO₂,¹ V-Mo-O,⁵ PMoH-5.75/SiO₂,⁶ Mo/MCM-41,⁷ a MoO₃(100) plane,⁸ and electrocatalysts,⁹ but the selectivities to methylal on those catalysts were very low. Hence, discovery of a new selective oxidation catalyst is the key issue to realize the direct methylal syn-

thesis from methanol, where three methanol molecules are incorporated into a methylal molecule. In this paper we wish to report the first selective synthesis of methylal by the catalytic methanol oxidation on a novel SbRe_2O_6 catalyst.

Three Sb-Re-O compounds, $\text{SbOReO}_4 \cdot 2\text{H}_2\text{O}$, SbRe_2O_6 and $\text{Sb}_4\text{Re}_2\text{O}_{13}$ were prepared according to the procedures reported elsewhere.¹⁰⁻¹⁴ For comparison, Sb_2O_3 - and SiO_2 -supported Re_2O_7 catalysts were also prepared by an incipient wetness impregnation method. Catalytic performances were examined in a conventional fixed-bed flow reactor at 1 atm ($\text{He}/\text{O}_2/\text{MeOH} = 86.3/9.7/4.0$ (mol%)).

The activities of various catalysts for methanol conversion and the selectivity toward methylal formation are shown in Table 1. Sb oxides such as Sb_2O_3 , Sb_2O_4 and Sb_2O_5 , a mechanical mixture of Re_2O_7 and Sb_2O_3 ($\text{Re}_2\text{O}_7 + \text{Sb}_2\text{O}_3$), and Re oxides supported on Sb_2O_3 and SiO_2 ($\text{Re}_2\text{O}_7/\text{Sb}_2\text{O}_3$ and $\text{Re}_2\text{O}_7/\text{SiO}_2$, respectively) showed no or negligible activities for the methylal formation at 573 K. $\text{Sb}_4\text{Re}_2\text{O}_{13}$ and $\text{SbOReO}_4 \cdot 2\text{H}_2\text{O}$ produced almost no methylal either. Only SbRe_2O_6 among the crystalline Sb-Re oxides synthesized thus far was active for the selective methanol oxidation to form methylal. The methylal selectivity was as high as 92.5% at a conversion of 6.5% (Table 1). 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.⁷ Further, the Mo/MCM-41 catalyst was rapidly deactivated due to a significant leaching of Mo species from the channels of MCM-41.⁷ On the other hand, no deactivation of the SbRe_2O_6 catalyst occurred after the 6 h reac-

Table 1. Methanol oxidation on several Sb-Re catalysts at 573 K^a and on other typical catalysts for comparison

Catalyst	Conv. /%	Selectivity /%							Ref.
		$\text{CH}_2(\text{OCH}_3)_2$	HCHO	CH_3OCH_3	HCOOCH_3	HCOOH	CO	CO_2	
$\text{SbRe}_2\text{O}_6^b$	6.5	92.5	0	6.3	1.2	0	0	0	This work
$\text{Sb}_4\text{Re}_2\text{O}_{13}$	0	0	0	0	0	0	0	0	This work
$\text{SbOReO}_4 \cdot 2\text{H}_2\text{O}$	4.7	1.0	0	99.0	0	0	0	0	This work
$\text{Re}_2\text{O}_7/\text{Sb}_2\text{O}_3$	2.5	7.4	49.8	42.7	0	0	0	0	This work
$\text{Re}_2\text{O}_7/\text{SiO}_2$	25.5	19.1	0	0.9	1.4	31.5	1.9	45.2	This work
$\text{Re}_2\text{O}_7 + \text{Sb}_2\text{O}_3$	1.4	23.6	0	76.4	0	0	0	0	This work
Sb_2O_3	0	0	0	0	0	0	0	0	This work
Sb_2O_4	0	0	0	0	0	0	0	0	This work
Sb_2O_5	1.3	trace	55.5	26.4	0	0	0	18.0	This work
PMoH-5.75/SiO ₂ ^c	c	56	17	7	20	0	0	0	6
2 mol%Mo/MCM-41 ^d	0.7	76.2	0	23.8	0	0	0	0	7
V/TiO ₂ ^e	c	40	60	0	0	0	0	0	1

^aCatalyst weight: 200 mg; Reactant composition: $\text{He}/\text{O}_2/\text{MeOH} = 86.3/9.7/4.0$ (mol%); GHSV = 10000 $\text{ml} \cdot \text{h}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$; The catalysts were pretreated under He at 573 K for 1 h before catalytic reaction. ^bSurface area of $\text{SbRe}_2\text{O}_6 = 0.5\text{--}1.0$ $\text{m}^2 \cdot \text{g}^{-1}$; The conversion of 6.5% corresponds to a rate of 1.06×10^{-3} $\text{mol} \cdot \text{h}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$. ^cReaction temperature = 513 K; Reactant composition: $\text{He}/\text{O}_2/\text{CH}_3\text{OH} = 85.2/10.3/4.5$ (mol%). The reaction rate was estimated as 0.52 $\text{mol} \cdot \text{h}^{-1} \cdot \text{g}_{\text{Mo}}^{-1}$. ^dReaction temperature = 503 K; Reactant composition: $\text{He}/\text{O}_2/\text{CH}_3\text{OH} = 76.0/16.3/7.7$ (mol%). The reaction rate was calculated to be 0.74×10^{-3} $\text{mol} \cdot \text{h}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$. ^eReaction temperature = 473 K; Reactant composition: $\text{He}/\text{O}_2/\text{CH}_3\text{OH} = 76/16.3/7.7$ (mol%). The reaction rate was estimated as 3.5×10^{-2} $\text{mol} \cdot \text{h}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$.

tion at 573 K. The methylal formation from methanol was also reported on PMoH-5.75/SiO₂ and V/TiO₂.^{1,6} The selectivities toward methylal on these catalysts were as low as 40–56%, even the activities were higher than SbRe₂O₆.

Figure 1 shows the catalytic methanol oxidation on SbRe₂O₆ under GHSV = 10000 ml·h⁻¹·g_{cat}⁻¹ and He/O₂/MeOH = 86.3/9.7/4.0 (mol%) as a function of reaction temperature. The 100% conversion of methanol corresponds to a reaction rate of 16.4 × 10⁻³ mol·h⁻¹·g_{cat}⁻¹. The reaction rate and the methylal selectivity increased with increasing temperature up to 573 K, where the selectivity to methylal reached maximum of 92.5%. Dimethyl ether was a main by-product whose formation decreased with temperature. An increase in the partial pressure of methanol resulted in a decrease in the reaction conversion, while the selectivity remained unchanged. The reaction rate was independent of O₂ concentration in the range of 1–10 mol%. The conversion of methanol on SbRe₂O₆ at 673 K increased to 86%, keeping a high selectivity of 85%. However, at this temperature SbRe₂O₆ partially decomposed to Sb₂O₄ and Re₂O₇ as proved by X-ray photoelectron spectroscopy (XPS), micro-confocal laser Raman spectroscopy (Raman), X-ray diffraction (XRD), and scanning electron microscopy (SEM).

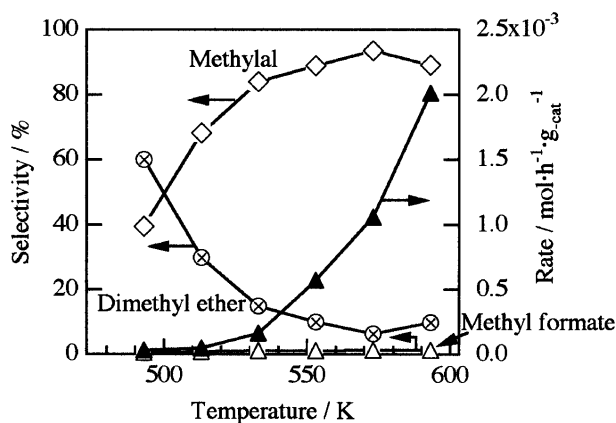


Figure 1. Catalytic methanol oxidation on SbRe₂O₆ as a function of reaction temperature; GHSV=10000 ml·h⁻¹·g_{cat}⁻¹; He/O₂/MeOH=86.3/9.7/4.0 (mol%).

The most active catalyst SbRe₂O₆ has a layer structure composed of mixed valent [Re₂O₆]³⁻ connecting with Sb³⁺ as shown in Figure 2.¹² SbRe₂O₆ grows as thin plate-like crystals

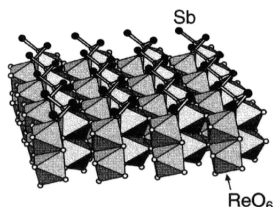


Figure 2. Structure of SbRe₂O₆ (100) plane

preferably exposing the (100) plane. No structural change in the bulk and surface was observed after the methanol oxidation at 573 K by means of XRD, SEM, XPS, and Raman.

A series of pulsed reactions of methanol in the absence of O₂ indicated that lattice oxygen atoms of the SbRe₂O₆ catalyst contributed to the selective catalysis. To examine the property of the lattice oxygen atoms, we investigated temperature-programmed desorption (TPD) of oxygen for the SbRe₂O₆ catalyst. The O₂-TPD experiments demonstrated that there existed two types of lattice oxygen species responsible for the selective methanol oxidation to methylal. The lattice oxygen atoms exhausted in the methylal formation were regenerated by O₂ during the catalytic methanol oxidation.

Recently, we demonstrated that SbOReO₄·2H₂O, SbRe₂O₆ and Sb₄Re₂O₁₃ were more or less active for the selective oxidation of isobutane and isobutylene to produce methacrolein.^{13,14} This is entirely different from the present results that only the SbRe₂O₆ compound showed the catalytic performance of methylal synthesis. The methylal formation from methanol may proceed on dual sites with redox and acidic properties.

In conclusion, the novel compound SbRe₂O₆ shows high performance for the selective catalytic oxidation of methanol to methylal. The selective oxidation is structure-specific. The high performance of SbRe₂O₆ may be ascribed to the Re-oxide species stabilized by the specific connection with Sb oxides at the crystal surface.

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