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 ($CH_2(OCH_3)_2$). Other known Sb-Re oxides, $Sb_4Re_2O_{13}$ and $SbOReO_4{\cdot}2H_2O$ 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 oxides[3] 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/TiO_2,[1] V-Mo-O,[5] PMoH-5.75/SiO_2,[6] Mo/MCM-41,[7] a $MoO_3(100)$ 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 synthesis 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, $SbOReO_4{\cdot}2H_2O$, $SbRe_2O_6$ and $Sb_4Re_2O_{13}$ 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 ($He/O_2/MeOH$ = 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 ($Re_2O_7 + Sb_2O_3$), and Re oxides supported on Sb_2O_3 and SiO_2 (Re_2O_7/Sb_2O_3 and Re_2O_7/SiO_2, respectively) showed no or negligible activities for the methylal formation at 573 K. $Sb_4Re_2O_{13}$ and $SbOReO_4{\cdot}2H_2O$ 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.
		$CH_2(OCH_3)_2$	HCHO	CH_3OCH_3	$HCOOCH_3$	HCOOH	CO	CO_2	
$SbRe_2O_6$[b]	6.5	92.5	0	6.3	1.2	0	0	0	This work
$Sb_4Re_2O_{13}$	0	0	0	0	0	0	0	0	This work
$SbOReO_4{\cdot}2H_2O$	4.7	1.0	0	99.0	0	0	0	0	This work
Re_2O_7/Sb_2O_3	2.5	7.4	49.8	42.7	0	0	0	0	This work
Re_2O_7/SiO_2	25.5	19.1	0	0.9	1.4	31.5	1.9	45.2	This work
$Re_2O_7+Sb_2O_3$	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]	e	40	60	0	0	0	0	0	1

[a] Catalyst weight: 200 mg; Reactant composition: $He/O_2/MeOH$ = 86.3/9.7/4.0 (mol%); GHSV = 10000 $ml{\cdot}h^{-1}{\cdot}g_{-cat}^{-1}$; The catalysts were pretreated under He at 573 K for 1 h before catalytic reaction. [b] Surface area of $SbRe_2O_6$ = 0.5-1.0 $m^2{\cdot}g^{-1}$; The conversion of 6.5% corresponds to a rate of 1.06×10^{-3} $mol{\cdot}h^{-1}{\cdot}g_{-cat}^{-1}$. [c] Reaction temperature = 513 K; Reactant composition: $He/O_2/CH_3OH$ = 85.2/10.3/4.5 (mol%). The reaction rate was estimated as 0.52 $mol{\cdot}h^{-1}{\cdot}g_{-Mo}^{-1}$. [d] Reaction temperature = 503 K; Reactant composition: $He/O_2/CH_3OH$ = 76.0/16.3/7.7 (mol%). The reaction rate was calculated to be 0.74×10^{-3} $mol{\cdot}h^{-1}{\cdot}g_{-cat}^{-1}$. [e] Reaction temperature = 473 K; Reactant composition: $He/O_2/CH_3OH$ = 76/16.3/7.7 (mol%). The reaction rate was estimated as 3.5×10^{-2} $mol{\cdot}h^{-1}{\cdot}g_{-cat}^{-1}$.

tion at 573 K. The methylal formation from methanol was also reported on PMoH-5.75/SiO_2 and V/TiO_2.[1,6] The selectivities toward methylal on these catalysts were as low as 40–56%, even the activities were higher than $SbRe_2O_6$.

Figure 1 shows the catalytic methanol oxidation on $SbRe_2O_6$ under GHSV = 10000 $ml·h^{-1}·g_{-cat}^{-1}$ and He/O_2/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 O_2 concentration in the range of 1–10 mol%. The conversion of methanol on $SbRe_2O_6$ at 673 K increased to 86%, keeping a high selectivity of 85%. However, at this temperature $SbRe_2O_6$ partially decomposed to Sb_2O_4 and Re_2O_7 as proved by X-ray photoelectron spectroscopy (XPS), mircro-confocal laser Raman spectroscopy (Raman), X-ray diffraction (XRD), and scanning electron microscopy (SEM).

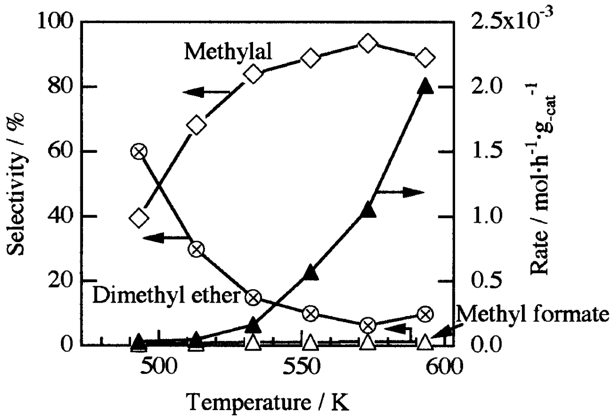

Figure 1. Catalytic methanol oxidation on $SbRe_2O_6$ as a function of reaction temperature; GHSV=10000 $ml·h^{-1}·g_{-cat}^{-1}$; He/O_2/MeOH=86.3/9.7/4.0 (mol%).

The most active catalyst $SbRe_2O_6$ has a layer structure composed of mixed valent $[Re_2O_6]^{3-}$ connecting with Sb^{3+} as shown in Figure 2.[12] $SbRe_2O_6$ grows as thin plate-like crystals 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.

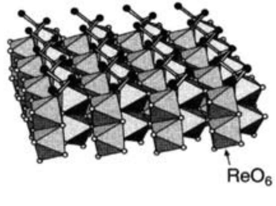

Figure 2. Structure of $SbRe_2O_6$ (100) plane

A series of pulsed reactions of methanol in the absence of O_2 indicated that lattice oxygen atoms of the $SbRe_2O_6$ 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 $SbRe_2O_6$ catalyst. The O_2-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 O_2 during the catalytic methanol oxidation.

Recently, we demonstrated that $SbOReO_4·2H_2O$, $SbRe_2O_6$ and $Sb_4Re_2O_{13}$ 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 $SbRe_2O_6$ 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 $SbRe_2O_6$ shows high performance for the selective catalytic oxidation of methanol to methylal. The selective oxidation is structure-specific. The high performance of $SbRe_2O_6$ may be ascribed to the Re-oxide species stabilized by the specific connection with Sb oxides at the crystal surface.

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References

1 J. M. Tatibouët, *Appl. Catal. A: General*, **148**, 213 (1997).
2 G. Busca, A. S. Elmi, and P. Forzatti, *J. Phys. Chem.*, **91**, 5236 (1987).
3 M. Ai, *J. Catal.*, **77**, 279 (1982).
4 N. Arora, G. Deo, I. E. Wachs, and A. M. Hirt, *J. Catal.*, **159**, 1 (1996).
5 J. M. Tatibouët and J. E. Germain, *Bull. Soc. Chim. Fr. I*, **9-10**, 343 (1980).
6 a) M. Fournier, A. Aouissi, and C. Rocchiccioli-Deltchff, *J. Chem. Soc. Chem. Commun.*, **1994**, 307. b) C. Rocchiccioli-Deltcheff, A. Aoussi, S. Launary, and M. Fournier, *J. Mol. Catal. A: Chemical*, **114**, 331 (1996).
7 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.*, **94**, 1495 (1998).
8 a) J. M. Tatibouët and J. E. Germain, *J. Catal.*, **72**, 375 (1981). b) J. M. Tatibouët, J. E. Germain, and J. C. Volta, *J. Catal.*, **82**, 240 (1983).
9 For example, K. Otsuka and I. Yamanaka, *Appl. Catal.*, **26**, 401 (1986).
10 W. T. A. Harrison, A. V. P. McManus, M. P. Kaminsky, and A. K. Cheetham, *Chem. Mater.*, **3**, 1631 (1993).
11 H. Watanabe and H. Imoto, *Inorg. Chem.*, **36**, 4610 (1997).
12 H. Watanabe, H. Imoto, and H. Tanaka, *J. Solid State Chem.*, **138**, 245 (1998).
13 E. C. Gaigneaux, H. Liu, H. Imoto, T. Shido, and Y. Iwasawa, *Topics in Catal.*, in press.
14 H. Liu, E. C. Gaigneaux, H. Imoto, T. Shido, and Y. Iwasawa, *J. Phys. Chem. B*, **104**, 2033 (2000).