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Author: Satoshi Kamiguchi Kazu Okumura Sayoko Nagashima Teiji Chihara

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Catalytic dehydrogenation of alcohol over solid-state molybdenum sulfide clusters with an octahedral metal framework

Satoshi Kamiguchi [a,b,*], Kazu Okumura[c], Sayoko Nagashima[d], and Teiji Chihara[d]

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[a] Advanced Catalysis Research Group, RIKEN Center for Sustainable Resource Science, 2-1 Hirosawa, Wako City, Saitama 351-0198, Japan

[b] Organometallic Chemistry Laboratory, RIKEN, 2-1 Hirosawa, Wako City, Saitama 351-0198, Japan

[c] School of Advanced Engineering, Kogakuin University, Nakano-machi, Hachioji City, Tokyo 192-0015, Japan

[d] Graduate School of Science and Engineering, Saitama University, Shimo-Okubo, Sakura-ku, Saitama City, Saitama 338-8570, Japan

* Corresponding author: Satoshi Kamiguchi

* Phone: (+81)48-467-1349

* Fax: (+81)48-467-9391

* E-mail: kamigu@riken.jp

* Address: RIKEN, Wako, Saitama 351-0198, Japan

Abstract

Solid-state molybdenum sulfide clusters with an octahedral metal framework, the superconducting Chevrel phases, are applied to catalysis. A copper salt of a nonstoichiometric sulfur-deficient cluster, $Cu_xMo_6S_{8-\delta}$ (x = 2.94 and $\delta \approx 0.3$), is stored in air for more than 90 days. When the oxygenated cluster is thermally activated in a hydrogen stream above 300 ºC, catalytic activity for the dehydrogenation of primary alcohols to aldehydes and secondary alcohols to ketones develops. The addition of pyridine or benzoic acid decreases the dehydrogenation activity, indicating that both a Lewis-acidic coordinatively unsaturated molybdenum atom and a basic sulfur ligand synergistically act as the catalytic active sites.

KEYWORDS: A. Chalcogenides, A. Inorganic compounds, A. Superconductors; D. Catalytic properties, D. defects.

1. Introduction

Solid-state molybdenum sulfide clusters with an octahedral metal framework, the Chevrel phases, are a common group of inorganic compounds. Studies on these clusters have focused mainly on their physical properties such as superconductivity and magnetism [1–3]. There are only a few reports on their use for catalysis [4–6], although these clusters do have some characteristic features as catalysts, for example: multimetal, multielectron systems; unique intermediate oxidation states of the metal atoms around 2^+; and high thermal stability expected from high synthesis temperatures (700–1000 °C). Considering these features, we have been studying the application of these clusters to various catalytic reactions such as the ring opening of tetrahydrofuran [7] and decomposition of methyl *tert*-butyl ether [8]. This paper describes the oxidant-free dehydrogenation of alcohols over the clusters with a sulfur-deficient molybdenum atom. The development of a new catalytic active site is also discussed.

2. Experimental

Solid-state molybdenum sulfide clusters $Cu_xMo_6S_{8-\delta}$ ($x = 2.94$, $\delta \approx 0.3$) (**1**) [9], $Mo_6S_{8-\delta}$ ($\delta \approx 0.4$) (**2**) [10], $Li_4Mo_6S_8$ (**3**) [11], and $Ni_2Mo_6S_8$ (**4**) [12] were synthesized according to the published procedures. The amounts of sulfur deficiency in **1** and **2** were determined by elemental analyses [7]. Crystals of these clusters were crushed and screened with a 150–200 mesh sieve. They were stored in air for more than 90 days before use as catalysts. The reactions were performed using a conventional continuous-flow microreactor operated at atmospheric pressure [13]. Typically, a weighed crystalline cluster sample (10 mg) of **1** stored in air was packed in a borosilicate glass tube (3 mm i.d.) and placed in the center of an electric furnace. The catalyst sample was initially activated from room temperature to a fixed temperature between 150 and 500 °C over 15 min in a hydrogen stream (1.2 L/h) and then held at this temperature for 45 min. Without changing the temperature, the reaction was initiated by adding 1-butanol (92 μL/h, 1.0 mmol/h) into the hydrogen stream using a syringe pump. The reaction was monitored every 20 min by sampling the reaction gas (1 mL) via a six-way valve held at 140 °C, followed by analysis using an online gas–liquid chromatography. The reactor effluent was frozen in a dry-ice trap for determination of material balance and subsequent analysis of the products. Catalytic reactions using the other catalysts were performed in the same way.

3. Results and Discussion

3.1 Catalytic reaction

The cluster, stored in air, was thermally activated in a hydrogen stream, followed by the reaction of 1-butanol at the activation temperature. A typical reaction profile at 300 ºC is plotted in Fig. 1. The catalytic activity slightly decreased with time, but the selectivity remained constant throughout the reaction. Dehydrogenation of 1-butanol to butyraldehyde was the main reaction, with 91% selectivity. In contrast, the selectivity for dehydration to butenes and dibutyl ether was very low, with 8 and 0.5% selectivity, respectively. The turnover frequency per Mo_6 cluster core over a period of 3–4 h was 26.2 h^{-1}, assuming that all the cluster cores were active. The material balance was 97% at 3–4 h after the start of the reaction. No appreciable changes in the X-ray diffraction pattern were observed after 3 h reaction with 1-butanol (see supplementary data, Fig. S1).

The catalytic activity for various alcohols over **1** is tabulated in Table 1. Primary alcohols such as ethanol and propanol were also selectively dehydrogenated to the corresponding aldehydes with 88–89% selectivity. Secondary alcohols such as 2-propanol and 3-pentanol were predominantly dehydrogenated to the corresponding ketones.

The catalytic activity of some molybdenum sulfide clusters and related compounds for the dehydrogenation of 1-butanol is tabulated in Table 2. All the clusters that were tested selectively catalyzed the dehydrogenation with 72–97% selectivity (entries 1–4). The activity decreased with a decreasing amount of sulfur deficiency (**1** ≈ **2** >> **3** ≈ **4**) [7]. When molybdenum metal and molybdenum disulfide were applied to the reaction, the dehydrogenation selectivities were <67% (entries 5 and 6). Some clusters with a Mo_6S_8 unit have been reported to decompose to molybdenum disulfide, molybdenum metal, or both, by thermal treatment under various atmospheres [6, 9, 14]. Even if these decomposed species were formed, they were not active in the reaction.

The effect of the reaction temperature on activity and selectivity over **1** at 3 h after the start of the reaction is presented in Fig. 2. Substantial catalytic activity appeared above 300 ºC and increased with increasing temperature with a maximum at 350 ºC: the conversion at this temperature was 46.3%, although it slightly decreased with time (38.3% at 4.67 h). The dehydrogenation to butyraldehyde was the main reaction over the temperature range 300–500 ºC, with >79% selectivity. At 350 ºC, the selectivity was highest (90.5%), and was almost constant with time (90.2% at 4.67 h).

3.2. Catalytic active site

We have investigated the activation process of **1**, using XRD patterns, thermogravimetric analyses, Fourier transform infrared spectra, X-ray photoelectron spectra, temperature programmed desorption of ammonia, and elemental analysis [7, 8]. A proposed mechanism for the activation can be summarized as follows. Upon storage in air for more than 90 days, **1** incorporates oxygen as an oxo ligand at the sulfur-deficient site on the cluster anion. When this oxygenated cluster is heated in a hydrogen stream, it releases the oxo ligand up to 300 °C, leading to the re-formation of sulfur-deficient **1** [7, 8]. As Fig. 2 shows, the dehydrogenation activity developed above 300 ºC, indicating the participation of the sulfur-deficient site or, in other words, the coordinatively unsaturated molybdenum atom in the reaction. When 1-butanol was allowed to react in the presence of 4 equivalents (eq) of pyridine at 300 °C, the conversion was reduced to 4%. This observation indicates that the Lewis acid site is catalytically active for the reaction.

It has been reported that acidic oxides (e.g., γ-Al_2O_3) are active for the dehydration of alcohols and basic oxides (e.g., MgO, CaO) for the oxidant-free dehydrogenation [15], where alcohol is adsorbed on metal as an alkoxide and on oxygen as a proton, followed by the elimination of an α-hydrogen of the alkoxide to afford a carbonyl compound and molecular hydrogen [16]. When 0.18 eq of benzoic acid was added to 1-butanol over **1**, the conversion decreased to 9%. The sulfur ligand in the activated **1** acts as a basic site; density functional theory (DFT) calculations of a discrete Mo_6S_8 cluster have shown that methanol is adsorbed on basic sulfur as a proton and on Lewis acidic molybdenum as a methoxide [17]. There are many reports on the reactivities of molybdenum sulfide clusters in which a sulfur ligand acts as a base [18].

Thus, both the Lewis acidic coordinatively unsaturated molybdenum cation and basic sulfide anion in **1** participate in the oxidant-free dehydrogenation of alcohols (Scheme 1). The catalytic activity of **2**–**4** is also attributable to the molybdenum cation and sulfide anion.

The dehydrogenation selectivity of the copper salt **1** was higher than that of the neutral cluster **2** (Table 2, entries 1 and 2). It has been reported that hydrotalcite-supported copper nanoparticle selectively catalyzes the dehydrogenation of alcohols [19]. In cluster **1**, two or three copper cations aggregate, with Cu–Cu distances of ca. 3 Å [20]. This copper aggregate was retained during the dehydrogenation of 1-butanol; the XRD pattern of **1** was the same before and after the reaction (Figure S1). Thus, the higher dehydrogenation selectivity of **1** is attributable to this copper aggregate.

4. Conclusions

Solid-state molybdenum sulfide clusters, the Chevrel phases, which are not metal oxide catalysts, catalyzed the oxidant-free dehydrogenation of alcohols. Both the Lewis-acidic coordinatively unsaturated molybdenum atom and basic sulfur ligand synergistically acted as the catalytic active sites. In this way, the Chevrel phases function as bifunctional acid–base catalysts.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version.

References

[1] R. Chevrel, M. Sergent, J. Prigent, J. Solid State Chem. 3 (1971) 515–519.

[2] Ø. Fischer, M. B. Maple, Superconductivity in Ternary Compounds I, Topics in Current physics 32, Springer, Berlin, 1982.

[3] M. B. Maple, Ø. Fischer, Superconductivity in Ternary Compounds II, Topics in Current physics 34, Springer, Berlin, 1982.

[4] M. Wakihara, H. Hinode, C. Inoue, Solid State Ionics 53–56 (1992) 413–417.

[5] K. F. McCarty, G. L. Schrader, Ind. Eng. Chem. Prod. Res. Dev. 23 (1984) 519–524.

[6] T. J. Paskach, G. L. Schrader, R. E. McCarley, J. Catal. 211 (2002) 285–295.

[7] S. Kamiguchi, K. Takeda, R. Kajio, K. Okumura, S. Nagashima, T. Chihara, J. Clust. Sci. 24 (2013) 559–574.

[8] S. Kamiguchi, Y. Seki, A. Satake, K. Okumura, S. Nagashima, T. Chihara, J. Clust. Sci. 26 (2015) 653–660.

[9] M. Rabiller-Baudry, M. Sergent, R. Chevrel, Mat. Res. Bull. 26 (1991) 519–526.

[10] E. Gocke, R. Schöllhorn, G. Aselmann, W. Müller-Warmuth, Inorg. Chem. 26 (1987) 1805–1812.

[11] R. J. Behlok, W. R. Robinson, Mat. Res. Bull. 18 (1983) 1069–1072.

[12] V. Harel-Michaud, G. Pesnel-Leroux, L. Burel, R. Chevrel, C. Geantet, M. Cattenot, M. Vrinat, J. Alloys Compd. 317–318 (2001) 195–200.

[13] S. Kamiguchi, M. Noda, Y. Miyagishi, S. Nishida, M. Kodomari, T. Chihara, J. Mol. Catal. A 195 (2003) 159–171.

[14] R. Chevrel, M. Sergent, J. Prigent, Mater. Res. Bull. 9 (1974) 1487–1498.

[15] A. Cimino, F. S. Stone, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 2, Wiley-VCH, Weinheim, 1997.

[16] Y. Shinohara, T. Nakajima, S. Suzuki, S. Mishima, H. Ishikawa, J. Chem. Software 4 (1998) 89–100.

[17] P. Liu, Y. Choi, Y. Yang, M. G. White, J. Phys. Chem. A 114 (2010) 3888–3895.

[18] M. Hidai, S. Kuwata, Y. Mizobe, Acc. Chem. Res. 33 (2000) 46–52.

[19] T. Mitsudome, Y. Mikami, K. Ebata, T. Mizugaki, K. Jitsukawa, K. Kaneda, Chem. Commun. (2008) 4804–4806.

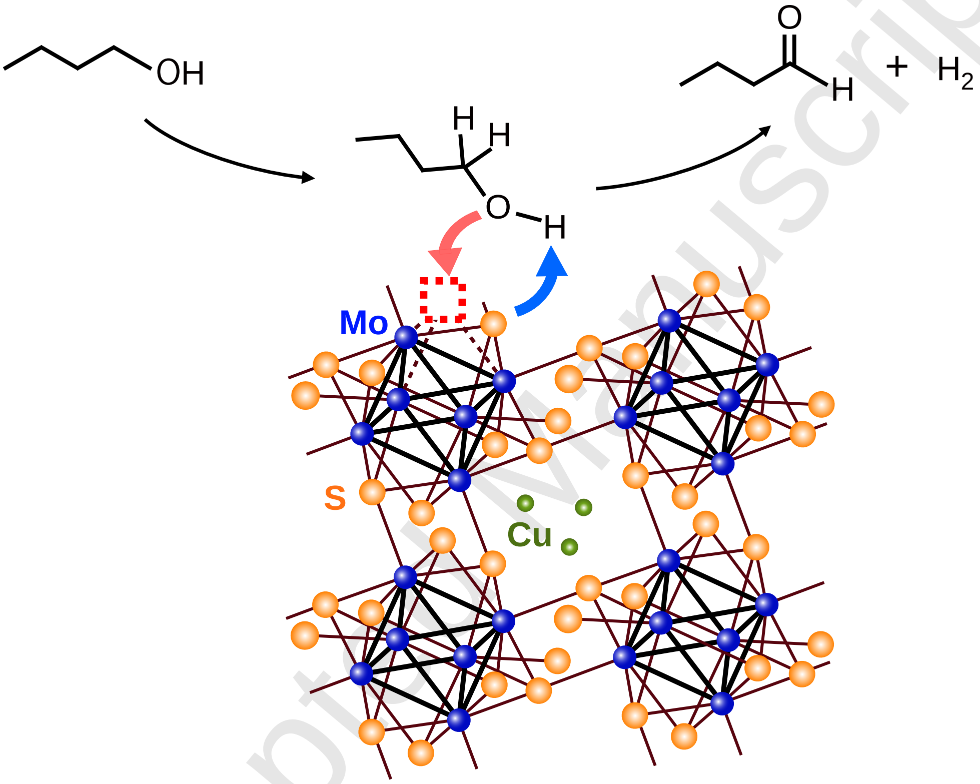
[20] K. Yvon, A. Paoli, Acta Crystallogr. B 33 (1977) 3066–3072.

Figure captions

Fig. 1 A typical reaction profile of 1-butanol dehydrogenation catalyzed by $Cu_xMo_6S_{8-\delta}$ (x = 2.94, $\delta \approx 0.3$) (**1**) in a hydrogen stream at 300 °C. Conversion = products/(products + recovered 1-butanol) × 100 (%); selectivity = product/(total amount of products) × 100(%). Legend: conversion (●); selectivity for butyraldehyde (○); selectivity for butenes (Δ), and selectivity for butyl ether (□).

Fig. 2 Effect of temperature on activity and selectivity in dehydrogenation of 1-butanol over $Cu_xMo_6S_{8-\delta}$ (x = 2.94, $\delta \approx 0.3$) (**1**) in a hydrogen stream at 3 h after the start of the reaction. Legend: conversion (●); selectivity for butyraldehyde (○); selectivity for butenes (Δ), and selectivity for butyl ether (□).

Graphical abstract



Highlights:

· Solid-state molybdenum sulfide clusters catalyzed the dehydrogenation of alcohol.

· The dehydrogenation proceeded without the addition of any oxidants.

· The catalytic activity developed when the cluster was activated at 300–500 ºC in H_2.

· The Lewis-acidic molybdenum atom and basic sulfur ligand were catalytically active.

· The clusters function as bifunctional acid–base catalysts.

Fig. 1

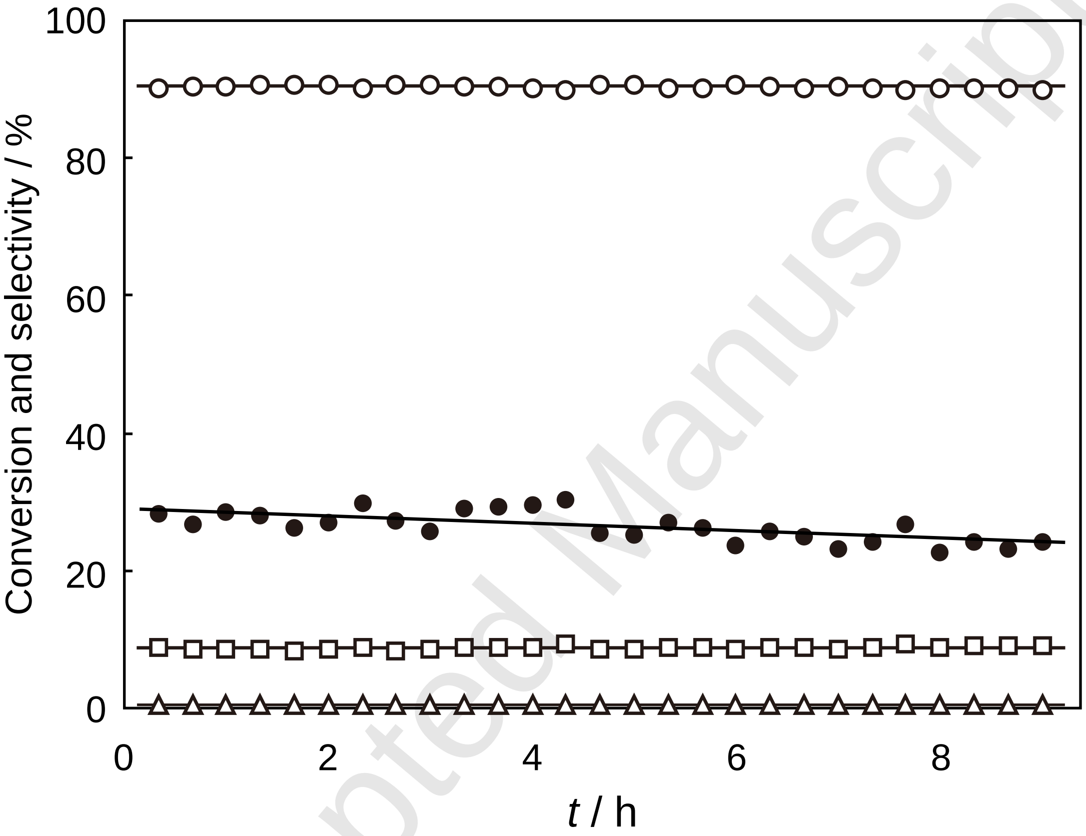
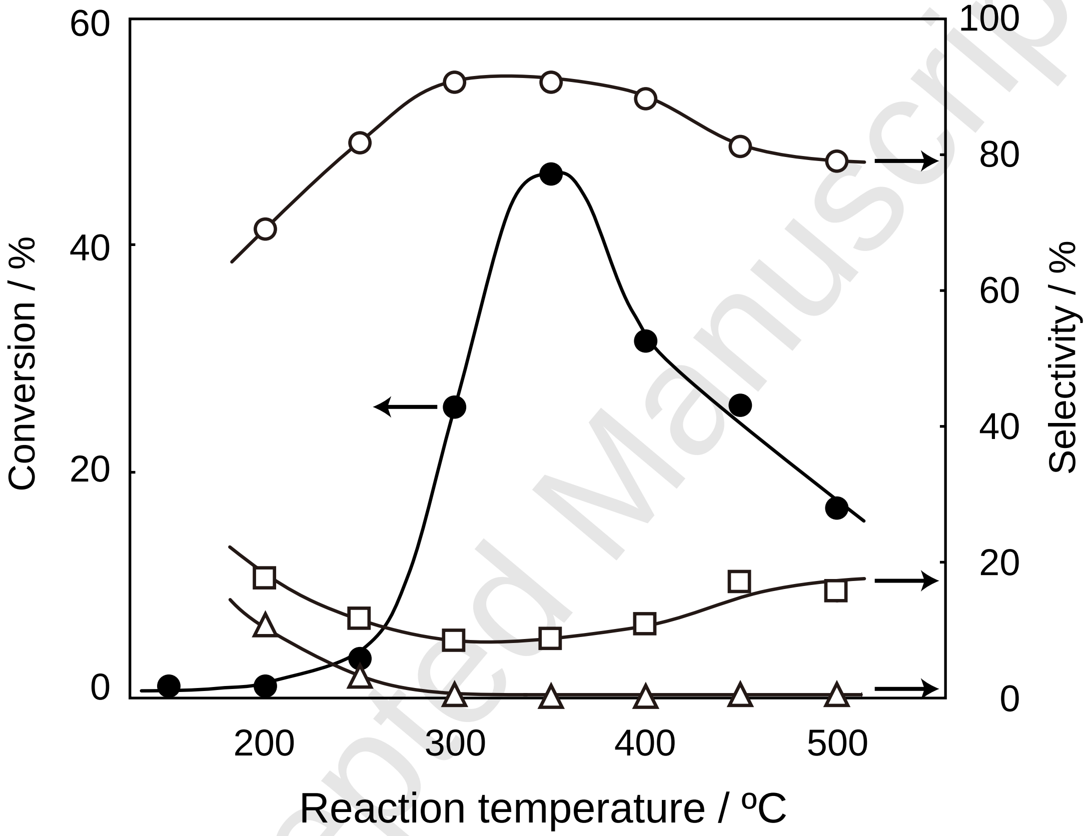


Fig. 2


60
40
20
0
100
80
60
40
20
0
Conversion / %
Selectivity / %
200
300
400
500
Reaction temperature / ºC

Scheme 1

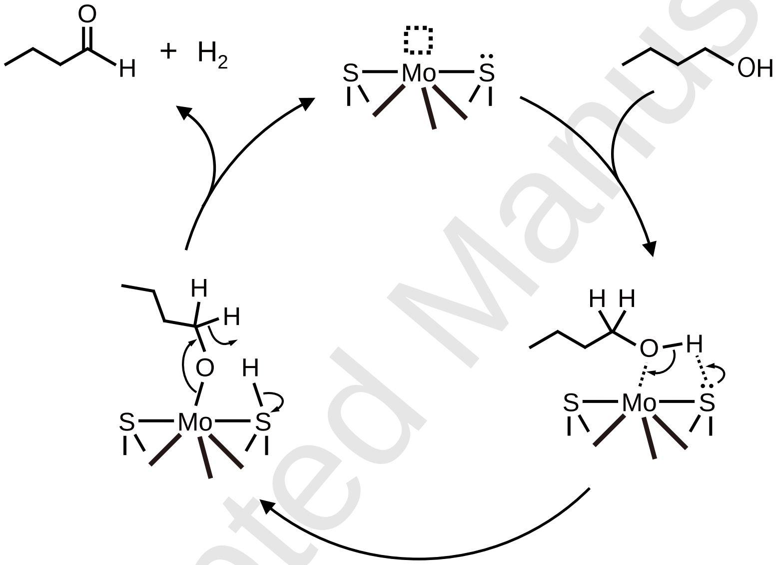


Table 1. Dehydrogenation of alcohols over $Cu_xMo_6S_8$ (**1**) at 300 ºC[a]

Alcohol	Conversion (%)	Selectivity (%)				
		Aldehyde	Ketone	Olefin	Ether	Others[b]
Ethanol	15.7	88.1	-	9.0	1.8	1.1
1-Propanol	13.2	89.3	-	9.9	0.0	0.8
1-Butanol	25.7	90.5	-	8.3	0.5	0.7
2-Propanol	72.8	-	82.0	17.2	0.1	0.7
3-Pentanol	63.0	-	54.2	44.8	0.0	1.0

[a] At 3 h after the start of the reaction. [b] Methane, ethylene, etc.

Table 2. Dehydrogenation of 1-butanol over various molybdenum sulfide cluster catalysts at 300 °C[a]

Entry	Catalyst	Conversion (%)	Selectivity (%)			
			Butyraldehyde	Butenes	Butyl ether	Others[b]
1	$Cu_xMo_6S_{8-\delta}$ (x = 2.94, $\delta \approx 0.3$) (**1**)	25.7	90.5	8.3	0.5	0.7
2	$Mo_6S_{8-\delta}$ ($\delta \approx 0.4$) (**2**)	24.0	74.9	24.1	0.5	0.5
3	$Li_4Mo_6S_8$ (**3**)	6.3	97.4	0.7	0.7	1.2
4	$Ni_2Mo_6S_8$ (**4**)	2.6	72.1	15.4	4.7	7.8
5	Mo metal[c]	3.7	52.6	12.1	2.4	32.9
6	MoS_2[d]	14.0	67.2	22.3	0.9	9.6
7	None	0.0	-	-	-	-

[a] At 3 h after the start of the reaction. [b] Methane, ethylene, etc. [c] Mo metal 80 mg. [d] MoS_2 50 mg.