Catalytic Hydrogenation and Dehydrogenation over Solid-state Rhenium Sulfide Clusters with an Octahedral Metal Framework

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When solid-state rhenium sulfide clusters with an octahedral metal framework are treated in a hydrogen stream above 250 °C, a catalytic activity for dehydrogenation of cyclohexanone to yield 2-cyclohexen-1-one and phenol develops. Dehydrogenation of cyclohexanol to cyclohexanone and hydrogenation of phenylacetylene to styrene also proceed. This catalytic behavior is the same as that of the platinum group metals. The catalytic activities are attributable to the partial loss of the sulfur ligands.

Various molecular and solid-state rhenium sulfide clusters with an octahedral metal framework have been synthesized. Studies on these clusters have focused mainly on syntheses, structures, and physical properties such as absorption, emission, redox behavior, and electrical conductivity.[1] These clusters have not been used as catalysts as far as we know, although rhenium oxide clusters with an octahedral metal framework have been applied to catalysis.[2] The rhenium sulfide clusters have multimetal multielectron systems and unique intermediate oxidation states of the metal atoms around 3^+. Thermal stability is expected for the clusters, because high temperatures (800–1450 °C) are required for the synthesis. Taking these features into consideration, attempts were made to apply the solid-state clusters to catalysis.

Solid-state rhenium-cluster compounds were synthesized according to the published procedures.[3] Crystals of the clusters were crushed and screened to 150–200 mesh. The reaction was performed in a conventional continuous-flow microreactor operated at atmospheric pressure. In a typical experiment, a weighed sample (30 mg, 0.017 mmol) of $Eu_2[Re_6S_8]S_{6/2}$ (**1**) 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 heated to 400 °C for 1 h in a hydrogen stream (600 mL/h), followed by introduction of cyclohexanone (52 µL/h, 0.50 mmol/h) into the hydrogen stream using a syringe pump at 400 °C. The catalytic activity decreased with time, while the selectivity leveled off after 3-h reaction. Dehydrogenation yielding 2-cyclohexen-1-one and phenol proceeded with a total selectivity of 91% at 9% conversion. The turnover frequency per Re_6-cluster core during a period of 3–4 h was $2.65\,h^{-1}$, assuming that all the cluster cores were active. The material balance was 95.3% at 3–4 h after the reaction had started.

Table 1 lists the catalytic activity of some rhenium sulfide clusters and related compounds at 3 h after the reactions had started at 400 °C. The clusters with alkali metals exhibited higher activity than **1**, presumably due to the presence of more easily removable S_2 bridges,[4] which are not involved in **1**. All of the clusters tested catalyzed dehydrogenation with a total selectivity of more than 90%, yielding 2-cyclohexen-1-one and phenol. In contrast, rhenium metal preferentially catalyzed degradation to yield gaseous products. Rhenium disulfide nonselectively catalyzed dehydrogenation, hydrogenation, and hydrodehydration. The selectivities of the rhenium sulfide clusters were different from those of rhenium metal and rhenium disulfide, indicating that the catalytic activity of the clusters does not arise from the formation of rhenium metal and rhenium disulfide, which are thermally stable phases in the Re–S system.[5] Table 1 also shows that Raney Ni and platinum metal selectively catalyzed the dehydrogenation. Thus, the rhenium clusters exhibited catalytic behavior similar that of the platinum group metals.

The effect of the reaction temperature on activity and selectivity over **1** is presented in Figure 1. Substantial catalytic activity developed above 250 °C. Dehydrogenation to 2-cyclohexen-1-one was the main reaction in the temperature range from 300 to 350 °C, and further dehydrogenation selectively yielding phenol proceeded in the temperature range from 400 to 425 °C. Above 450 °C, degradation of alicyclic ring may predominantly occur to yield gaseous products.

Table 1. Dehydrogenation of cyclohexanone over rhenium sulfide cluster catalysts[a]

Catalyst	W/F /g h mol^{-1}	Conversion /%[b]	Selectivity/%[c]						
			Dehydrogenation			Hydrogenation	Hydrodehydration	Degradation products[d]	Other products[e]
			2-Cyclohexen-1-one	Phenol	(Total)	Cyclohexanol	Cyclohexene		
$Cs_4[Re_6S_8]SS_{2/2}(S_2)_{3/2}$	60	37.7	17.0	82.1	99.1	0.3	0.1	0.4	0.1
$K_4[Re_6S_8]S_{4/2}(S_2)_{2/2}$	60	32.9	28.7	69.9	98.6	0.9	0.0	0.4	0.1
$Eu_2[Re_6S_8]S_{6/2}$ (**1**)	60	9.0	26.9	63.9	90.8	1.1	3.2	2.0	2.9
Re metal	60	5.6	24.2	4.9	29.1	9.2	9.3	42.8	9.6
ReS_2	60	15.2	21.4	25.8	47.2	21.4	20.5	0.0	10.9
Raney Ni[f]	4	23.4	11.0	80.5	91.5	0.6	1.2	5.0	1.7
Pt/C[g]	400	17.0	8.8	77.5	86.3	1.5	6.1	2.2	3.9
None	—	0.5	19.9	0.0	19.9	4.8	8.1	58.9	8.3

[a] After treatment of catalyst (150–200 mesh, 30 mg) in a hydrogen stream (600 mL/h) at 400 °C for 1 h, reaction was initiated by introduction of cyclohexanone (52 µL/h, 0.50 mmol/h) into the hydrogen stream at 400 °C. [b] Conversion = products/(products + recovered cyclohexanone) × 100% at 3 h after the reaction had commenced. [c] Selectivity = product/(total amount of products) × 100% at 3 h after the reaction had commenced. [d] Methane, ethylene, etc. [e] Cyclohexane, benzene, etc. [f] Raney Ni (2 mg) diluted with quartz sand (18 mg). [g] 30 wt % Pt on charcoal (30–40 mesh, 200 mg).

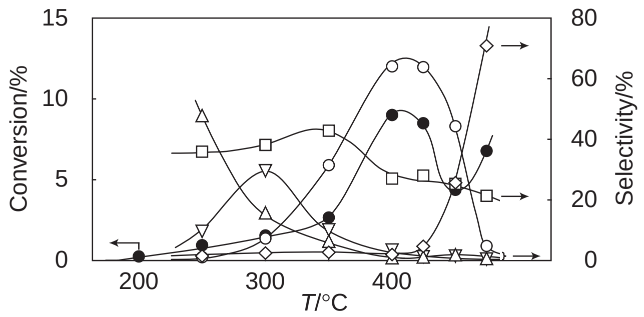

Figure 1. Temperature effect on the reaction of cyclohexanone over $Eu_2[Re_6S_8]S_{6/2}$ (**1**) in a hydrogen stream at 3 h after the reaction started. Both initial treatment and reaction temperatures were altered concomitantly. Other conditions are the same as in Table 1. Conversion = products/(products + recovered cyclohexanone) × 100%, selectivity = product/(total amount of products) × 100%. Conversion of cyclohexanone (●), selectivity for 2-cyclohexen-1-one (□), selectivity for phenol (○), selectivity for cyclohexanol (△), selectivity for cyclohexene (▽), and selectivity for degradation products (◇).

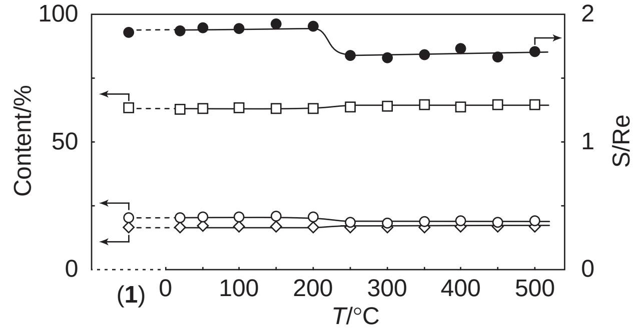

Figure 2. Analytical data for $Eu_2[Re_6S_8]S_{6/2}$ (**1**) treated at various temperatures in a hydrogen stream for 1 h. Analytical data for intact **1** are also plotted. Eu (◇), Re (□), S (○), and the ratio of S/Re (●).

When **1** was heated progressively under hydrogen, evolution of hydrogen sulfide was detected around 250 °C. The analytical data of **1** treated at various temperatures under hydrogen for 1 h are shown in Figure 2. The sulfur content and consequently the relative amount of sulfur to rhenium decreased at 250 °C, at which temperature the catalytic activity developed. The experimental formula of the sample treated at 400 °C was $Eu_{2.0}Re_{6.0}S_{10.3}$. The Raman spectra of the treated cluster samples are shown in Figure 3. The peak at 309 cm^{-1} assignable to the breathing motion of the Re_6 octahedron[6] was retained up to 500 °C, indicating that the Re_6-cluster framework was intact throughout the treatment. Powder X-ray diffraction (XRD) patterns of the treated cluster samples remained unchanged up to 500 °C, which demonstrates that the crystal structure of **1** did not change throughout the treatment. X-ray photoemission spectrum (XPS) data showed that the electronic state of rhenium was not changed after the treatment at 400 °C. No appreciable changes were observed in the analytical data, the Raman spectrum, and the XRD pattern of **1** after the 3-h reaction with cyclohexanone at 400 °C. From these results, the development of an active site on the rhenium cluster **1** can be proposed as follows. The sulfur ligand is partially removed as hydrogen sulfide to yield a coordinatively unsaturated rhenium metal atom by thermal treatment in a hydrogen stream above 250 °C. The cluster framework containing the unsaturated atom is protected in the crystal structure of the solid-state cluster at temperatures as high as 500 °C. The unsaturated rhenium atom could be isoelectronic with the platinum group metals by taking some electrons from the resulting sulfur ligands. This active site is different from those of reported rhenium sulfide catalysts: rhenium and sulfur atoms of Re_2S_2 moiety in the rhenium disulfide layer structure,[7] oxygen atoms of a sulfur dioxide ligand in a trinuclear cluster $[(Re_3S_3(SO_2))Cl_6(PMe_2Ph)_3]$,[8] and a hydroxo ligand formed by hydrolysis of the chloro ligands of a trinuclear cluster $Re_3S_7Cl_4$ in aqueous solution.[9]

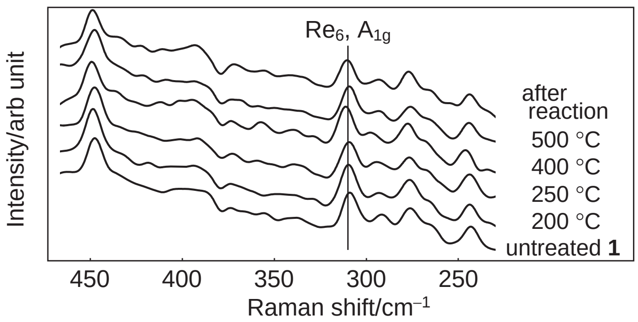

Figure 3. Raman spectra of $Eu_2[Re_6S_8]S_{6/2}$ (**1**) treated at various temperatures in a hydrogen stream for 1 h.

When **1** (200 mg) was applied to the hydrogenation of phenylacetylene (55 µL/h, 0.50 mmol/h) under the same reaction conditions, hydrogenation proceeded to yield styrene with 86.7% selectivity at 3.3% conversion. Cyclohexanol (53 µL/h, 0.50 mmol/h) also reacted over **1** (10 mg), producing the dehydrogenation product cyclohexanone with 64.6% selectivity at 20.0% conversion. These selectivities of **1** have also been reported for the platinum group metals.[10,11] Thus, the rhenium sulfide clusters served as platinum-like catalysts.

References

1 J.-C. P. Gabriel, K. Boubekeur, S. Uriel, P. Batail, *Chem. Rev.* **2001**, *101*, 2037; Y. Sasaki, *J. Nucl. Radiochem. Sci.* **2005**, *6*, 145.
2 N. Viswanadham, T. Shido, T. Sakaki, Y. Iwasawa, *J. Chem. Phys. B* **2002**, *106*, 10955.
3 W. Bronger, M. Spangenberg, *J. Less-Common Met.* **1980**, *76*, 73; W. Bronger, H.-J. Miessen, D. Schmitz, *J. Less-Common Met.* **1983**, *95*, 275; W. Bronger, M. Loevenich, D. Schmitz, T. Schuster, *Z. Anorg. Allg. Chem.* **1990**, *587*, 91.
4 M. R. DuBois, M. C. VanDerveer, D. L. DuBois, R. C. Haltiwanger, W. K. Miller, *J. Am. Chem. Soc.* **1980**, *102*, 7456.
5 C. Fischer, S. Fiechter, H. Tributsch, G. Reck, B. Schultz, *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96*, 1652.
6 T. G. Gray, C. M. Rudzinski, E. E. Meyer, R. H. Holm, D. G. Nocera, *J. Am. Chem. Soc.* **2003**, *125*, 4755.
7 V. M. Belousov, G. I. Korenyako, O. M. Negomedzyanova, *React. Kinet. Catal. Lett.* **1982**, *21*, 371.
8 T. Saito, T. Sunaga, N. Sakai, Y. Nakamura, S. Yamamoto, D. Iriuchijima, K. Yoza, *Inorg. Chem.* **2005**, *44*, 4427.
9 V. M. Belousov, T. A. Pal'chevskaya, S. V. Volkov, V. L. Kolesnichenko, L. V. Bogutskaya, S. P. Sharavskaya, *Theor. Exp. Chem.* **1993**, *28*, 194.
10 M. Freifelder, in *Practical Catalytic Hydrogenation*, Wiley-Interscience, New York, **1971**.
11 M. V. Landau, S. B. Kogan, D. Tavor, M. Herskowitz, J. E. Koresh, *Catal. Today* **1997**, *36*, 497.

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