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Catalytic dehydrogenation of aliphatic amines to nitriles, imines, or vinylamines and dealkylation of tertiary aliphatic amines over halide cluster catalysts of group 5 and 6 transition metals

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Abstract

A molybdenum halide cluster, $(H_3O)_2[(Mo_6Cl_8)Cl_6] \cdot 6H_2O$, with an octahedral metal framework was used as a catalyst in a gas-flow reactor under hydrogen or helium. Diethylamine started to react above 300 °C, and dehydrogenation to *N*-ethylideneethylamine proceeded selectively above 350 °C. Dibutylamine yielded the corresponding dehydrogenation product, and pyrrolidine and piperidine were dehydrogenated to 1-pyrroline and 2,3,4,5-tetrahydropyridine. Dehydrogenation of primary amines yielded the corresponding nitriles and the condensation product *N*-alkylidenealkylamine. Tripropylamine and tributylamine were dehydrogenated to yield, for the most part, *N*-vinyldialkylamines. In contrast, triethylamine was dealkylated to diethylamine. Thus, the halide cluster exhibited a characteristic catalysis for aliphatic amines: nitrogen-bonded hydrogens were removed completely to yield nitrile or imine, and when there was no such hydrogen, a neighboring hydrogen or the nitrogen-bonded alkyl group was removed. Niobium, tantalum, and tungsten chloride clusters of the same metal framework were also active catalysts for dealkylation and dehydrogenation of diethylamine.

Keywords: Dehydrogenation; Dealkylation; Amine; Imine; Vinylamine; Ethylamine; Diethylamine; Triethylamine; Halide cluster; Molybdenum chloride

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1. Introduction

Halide clusters, which have a highly symmetrical and aesthetically pleasing molecular structure [1], have been attractive catalyst candidates for more than 140 years [2]. One possibility for understanding the nature of the catalytic activity of halide clusters is provided by a physicochemical investigation of activated halide clusters. Another possibility is to apply the catalyst to many compounds and to search for new reactions catalyzed by halide clusters; a comprehensive view of the catalyst can be obtained by comparison with other catalysts. Some reactions that are catalyzed by halide clusters are known to proceed over conventional acid catalysts: the isomerization of olefins [3], the dehydrohalogenation of halogenated alkanes [4], the isomerization of diethylbenzenes [5], the dehydration of alcohols [6], and the decomposition of phenyl acetate to phenol and ketene [7]. When ethylbenzene reacted in the presence of a halide cluster, hydrogenolysis proceeded under hydrogen to yield toluene and benzene. Under helium, dehydrogenation occurred, yielding styrene. This variable selectivity is the same as that over the platinum-group metal catalysts [8]. Selective dehydrogenation and dealkylation of aliphatic amines, another novel feature of cluster catalysis, is the subject of this report.

Catalytic dehydrogenation of amines has been investigated extensively, and the dehydrogenation of primary amines usually gives the corresponding nitriles. Most re-

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ported reactions are oxidative dehydrogenations: an $[Os(OH)_2O_4]^{2-}$ catalyst combined with ferric ion as an oxidizing reagent [9], Rh-porphyrine with dioxygen [10], $[Ru(OH)_2O_3]^{2-}$ with the oxidizing reagent $[S_2O_8]^{2-}$ [11], and $NiSO_4$ with $[S_2O_8]^{2-}$ [12]. Strong oxidation conditions occasionally lead to further oxidation: butylamine is oxidized to butylamide by $RuCl_3$ in the presence of dioxygen [13] or to butyric acid by RuO_4 in the presence of $[S_2O_8]^{2-}$ [14]. A Schiff base can be obtained by dehydrogenation of a primary amine to the imine followed by condensation with the amine: benzylamine is converted to *N*-benzylidenebenzylamine over Mo–V-heteropoly acid in the presence of O_2 [15]. On the other hand, catalytic dehydrogenation without oxidizing reagents is rare: molten Zn or Ga metal [16] and Ga–MFI zeolite [17] have been used as catalysts in gas-phase reactions. In toluene solution, $RhH(PPh_3)_3$ reversibly catalyzes dehydrogenation [18].

There are several reports on the catalytic and stoichiometric dehydrogenation of activated secondary amines, Ar–CH_2–NH–R (Ar = aryl, R = alkyl or aryl) or R–CH_2–NH–Ar (R = alkyl, Ar = aryl). The dehydrogenation product is unique, and, hence, selective reaction can be readily achieved as long as C–N bond cleavage does not occur [19]. In contrast, reports on aliphatic secondary amines are few. Catalytic dehydrogenation of diethylamine to *N*-ethylideneethylamine has been reported only for a dihydridoiridium complex $IrH_2(\eta^3\text{-}2,6\text{-}(t\text{-}Bu_2PCH_2)_2C_6H_3)$ [20] and Mo-heteropoly acid [21].

There are a limited number of examples of dehydrogenation of aliphatic tertiary amines. Triethylamine is catalytically dehydrogenated to *N*-vinyldiethylamine by the dihydridoiridium complex in the presence of a hydrogen acceptor such as 3,3-dimethyl-1-butene [22]. However, a solid acid–base hybrid catalyst, ZrO_2 or silica-alumina/MgO, converts triethylamine to acetonitrile and forms ethylene [23]. Thus, catalytic dehydrogenation of aliphatic amines is rare, particularly in the gas phase. Furthermore, there are no reports of halogen compounds being used as the catalyst.

2. Experimental

2.1. Materials and characterization

The cluster complexes $[(Nb_6Cl_{12})Cl_2(H_2O)_4] \cdot 4H_2O$ [24], $(H_3O)_2[(Mo_6Cl_8)Cl_6] \cdot 6H_2O$ (**1**) [25], $[(Mo_6Br_8)(OH)_4(H_2O)_2]$ [26], $[(Ta_6Cl_{12})Cl_2(H_2O)_4] \cdot 4H_2O$ [24], and $(H_3O)_2[(W_6Cl_8)Cl_6] \cdot 6H_2O$ [27] were prepared according to published procedures, followed by repeated recrystallization to yield well-formed single crystals. By heating **1** at a rate of 100 °C/h to 200 °C followed by holding at 200 °C for 6 h under vacuum, we obtained the solid-state cluster $[Mo_6Cl_8]Cl_2Cl_{4/2}$ (Mo_6Cl_{12}, **2**) [24], where Cl_8 denotes eight face-capping ligands, Cl_2 denotes two terminal ligands, and $Cl_{4/2}$ denotes four intercluster-bridging ligands [28,29]. Commercial crystalline, Re_3Cl_9, was used without further purification. The crystals were crushed until they could be passed through a 150-mesh screen but not a 200-mesh screen. Ethylamine was used as a THF solution (2.0 mol/l; Aldrich). The other organic substrates were commercial products (> 99%) and were used as purchased.

Mo *K*-edge EXAFS spectra were recorded in transmission mode at BL-10B of KEK-PF with a Si(311) channel-cut crystal monochromator and ionization chambers. The energy of the X-ray was calibrated with the use of an Mo foil. EXAFS data were analyzed with the UWXAFS package [30]. After background subtraction with AUTOBK [31], k^3-weighted EXAFS functions were Fourier-transformed into *R*-space and fitted in *R*-space. The *k* and *R* ranges for Fourier transformation and curve fitting were 30–160 nm^{-1} and 0.1–0.4 nm, respectively. The backscattering amplitude and phase-shift functions of Mo–Mo were calculated from **1** with the FEFF8.0 code; curve fitting was done with the FEFFIT code [32].

Raman spectra of the cluster samples in glass reaction tubes were recorded in situ on a Kaiser Optical Systems HoloLab 5000 Spectrometer with the use of a Nd-YAG laser operating at $\lambda = 532$ nm with a 7.6-mm focusing lens. The data counts were accumulated 30 times over 1-s intervals. Then the cluster samples were transferred to an airtight sample holder in a glove box, and powder X-ray diffraction (XRD) was performed on 30-mg samples with a MacScience MXP21TA-PO X-ray diffractometer and Cu-K_α radiation at a scan rate of 2° min^{-1}.

The trapped reaction products were analyzed with a Hewlett–Packard 5890 Series II gas chromatograph coupled with a Jeol Automass System II analyzer with a DB-1 capillary column (GC/MS). Most of the products were identified by comparing them with commercial samples with the use of a GL Science 353B gas chromatograph (GLC) fitted with a flame ionization detector with DB-1 and DB-WAX capillary columns. The other products were isolated with the use of a GLC fitted with a thermal conductivity detector and determined by NMR and mass spectrometry.

The catalytic activities were evaluated with an on-line Shimadzu 14B GLC. This was fitted with a flame ionization detector, an Amipack 141 packed column (1.5 m × 3 mm) to study the reactions of tripropylamine and tributylamine, and a Unicarbon B-2000 packed column (5 m × 3 mm) for the other reactions. The gaseous products were identified by on-line GLC with a Unipak-S packed column (3 m × 3 mm).

2.2. Apparatus and procedures

The gas flow reactions were carried out in a conventional apparatus [3]. The gas flow rate was controlled by a flow regulator at ambient pressure, and the gas was introduced into a temperature-controlled stainless-steel tube (length = 3 m, i.d. = 2 mm), which was used to heat the carrier gas to the same temperature as the reactor. The general procedure consisted of packing a known mass of the cluster complex into an electrically heated vertical tubular borosilicate glass reactor (i.d. = 3 mm) with the aid of quartz glass wool. Immediately before the reaction, catalyst pretreatment was performed in situ in a stream of the gas for 1 h at the operating temperature. Then the liquid reactant was introduced at a controlled rate with a motor-driven glass syringe pump through a T-joint attached to the front of the reactor vessel. The products were introduced every 30 min into a temperature-controlled gas sampler (1 ml) connected to a six-way valve, which was kept at 120 °C, and were analyzed with the on-line GLC. The reactor effluent was frozen in a dry-ice trap for subsequent analysis, which was performed with a capillary column GLC.

In a typical experiment, a weighed cluster sample of $(H_3O)_2[(Mo_6Cl_8)Cl_6] \cdot 6H_2O$ (**1**) (30 mg) was placed in the glass reaction tube surrounded by a closely fitting copper tube in the center of an electric furnace. The catalyst sample was heated from room temperature to 400 °C and was maintained at that temperature for 1 h in a stream of hydrogen (600 ml/h) before kinetic measurement. After 15 min, the temperature reached the set point. We initiated the reaction by feeding undiluted diethylamine (0.20 ml/h, 1.9 mmol/h) into the stream of hydrogen. The relative ratio of hydrogen to diethylamine was 13. Analyses of the trapped products showed that the material balance was 90.8% (3–4 h) and that 0.33% of the diethylamine was dealkylated to ammonia. The conversions and selectivities reported here are based on the data from the on-line GLC analysis. Ethylene was ignored; only nitrogen-containing organic compounds were taken into account. In the experiment with diethylamine and the catalyst **1**, the conversion was 20.5% and the selectivity for ethylideneethylamine 72.0% 3 h after the reaction started. The conversion was proportional to the amount of catalyst but independent of the flow rates of hydrogen carrier gas and diethylamine as long as the latter was lower than 0.8 ml/h (7.6 mmol/h); the reaction showed first-order kinetics. Subsequent experiments were performed in this flow region.

3. Results and discussion

3.1. Activation of the halide cluster

So that we would be able to ascribe the catalytic activity and selectivity to the halide cluster, the clusters were not supported on solid adsorbents but were used as crushed crystals, albeit at the expense of catalytic efficiency. The powdered crystals of $(H_3O)_2[(Mo_6Cl_8)Cl_6] \cdot 6H_2O$ (**1**) were packed into a glass reaction tube and heated in a stream of hydrogen or helium for 1 h. We started the reaction by introducing diethylamine into the stream at the same temperature. Fig. 1 shows a typical reaction profile with product distribution at 400 °C in a hydrogen or helium stream. In the hydrogen stream, the reactivity leveled off after 2 h and selectivity hardly changed, with the dehydrogenation product *N*-ethylideneethylamine in 72% selectivity. On the other hand, the reactivity in a stream of helium decreased with time; selectivity also changed, with the dehydrogenation product showing more than 60% selectivity at the initial stage of the reaction. In both hydrogen and helium streams, some dealkylation occurred, yielding ethylamine.

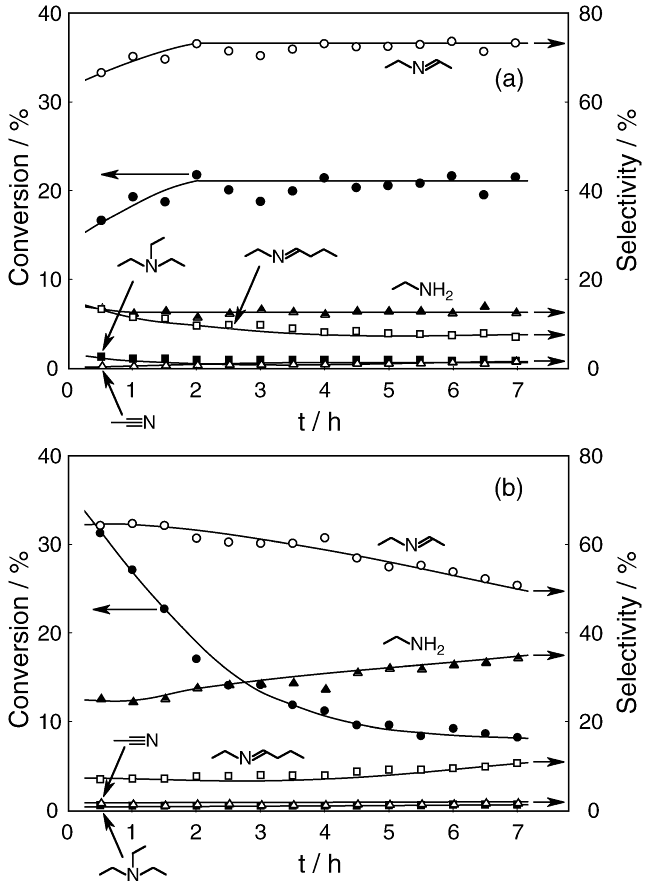

Fig. 1. Typical reaction profile of diethylamine dehydrogenation catalyzed by $(H_3O)_2[(Mo_6Cl_8)Cl_6] \cdot 6H_2O$ (**1**) in a (a) H_2 and (b) He stream. Following treatment of **1** (30 mg) in the gas stream (600 ml/h) at 400 °C for 1 h, reaction was started by introduction of diethylamine (0.20 ml/h) to the stream at the same temperature. Conversion = products/(products + recovered diethylamine) × 100 (mol%). Selectivity = product/(total amount of products) × 100 (mol%).

Fig. 2 shows catalytic activities of **1** at various temperatures. Treatment above 250 °C in a hydrogen stream or above 300 °C in a helium stream resulted in catalytic activity. Cluster **1** is a coordinatively saturated stable compound and has no metal–metal multiple bonds, and hence the intact cluster is not catalytically active. Thermal treatment resulted in catalytic activity. The activity under hydrogen reached steady state after 3 h, whereas that under helium decreased with time. The higher the reaction temperature, the greater the decrease in activity. The activity in a hydrogen stream was about twice as high as that in a helium stream at the same temperature. Three hours after the start of the reactions, the product contained, respectively, about 1.8 and 3.3 mol% ethylene, based on reacted diethylamine in the hydrogen and helium streams. Formation of coke would slow down the reaction, particularly in a helium stream at higher temper-

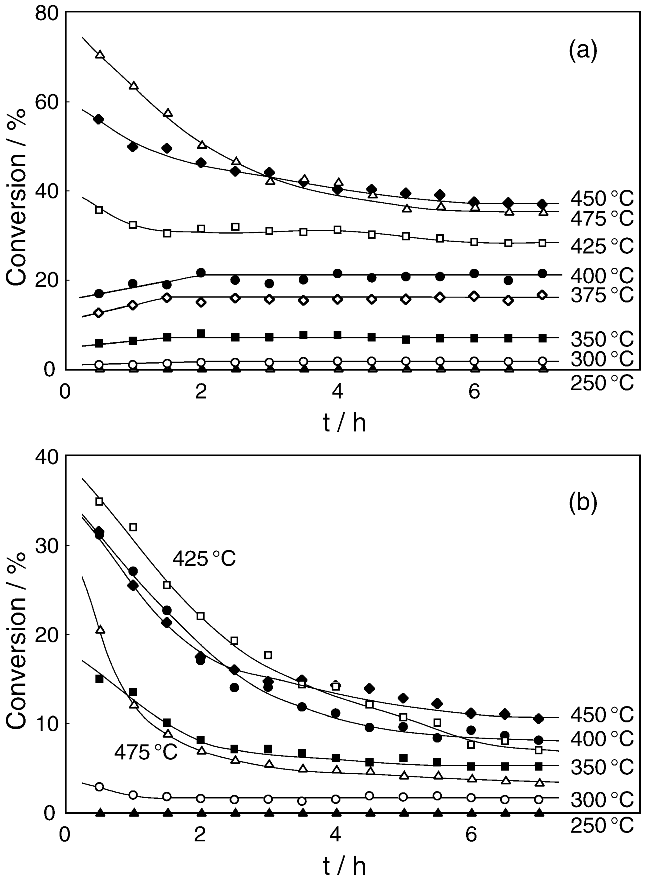

Fig. 2. Catalytic activity of $(H_3O)_2[(Mo_6Cl_8)Cl_6] \cdot 6H_2O$ (**1**) for diethylamine at various temperatures in a (a) H_2 and (b) He stream. After treatment of **1** at various temperatures for 1 h in the gas stream, reactions were started at the same temperatures. Other reaction conditions are the same as given in Fig. 1. Conversion = products/(products + recovered diethylamine) × 100 (mol%).

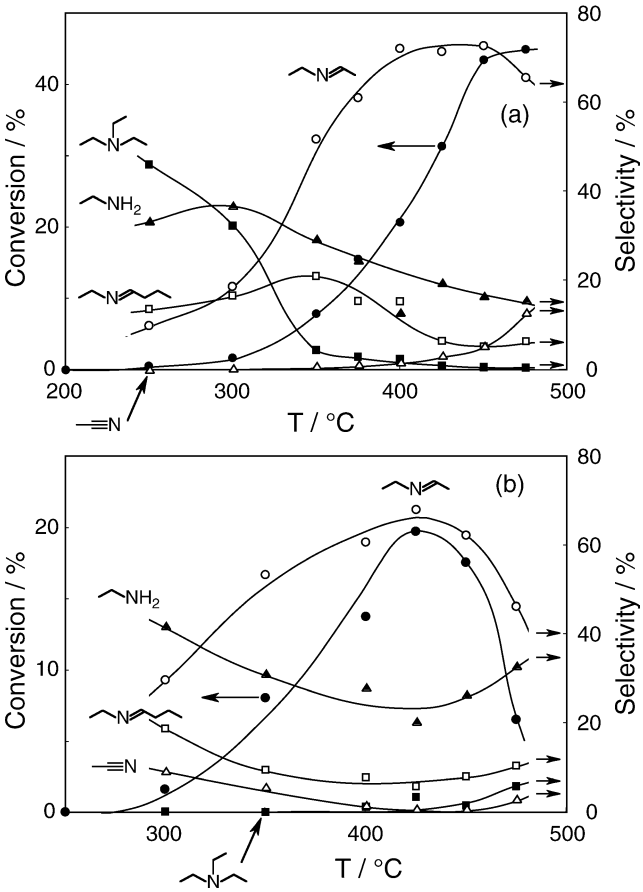

Fig. 3. Temperature effect on reactivity and selectivity of diethylamine over $(H_3O)_2[(Mo_6Cl_8)Cl_6] \cdot 6H_2O$ (**1**) in a (a) H_2 and (b) He stream 3 h after reaction started. Other reaction conditions are the same as given in Figs. 1 and 2. Conversion = products/(products + recovered diethylamine) × 100 (mol%). Selectivity = product/(total amount of products) × 100 (mol%).

atures. It is well known that high-temperature processes for the catalytic conversion of hydrocarbons are often accompanied by deposition of hydrogen-deficient coke [33], and that the deposition of these products causes a decrease in catalytic activity [34]. For example, a decrease in catalytic activity is reported for ethylbenzene dehydrogenation, in which carbonaceous products are formed from the ethylene by-product [33].

The effect of the reaction temperature on reactivity and product selectivity is presented in Fig. 3. Under hydrogen, the reactivity increased with increasing temperature and the selectivity varied with the temperature. At lower temperatures, disproportionation yielding ethylamine and triethylamine was predominant; at higher temperatures dehydrogenation providing *N*-ethylideneethylamine was the main reaction. Dehydrogenation of the produced ethylamine to acetonitrile was also obvious at higher temperatures. Under helium the catalytic activity was about half that under hydrogen at temperatures lower than 425 °C. Dealkylation yielding ethylamine was noticeable at lower temperatures, and maximum selectivity (69%) for *N*-ethylideneethylamine was reached at 425 °C. The selectivity thus changed with temperature. A similar change in product selectivity with temperature was observed in the reaction of *p*-diethylbenzene over **1**: *p*-diethylbenzene was dehydrogenated to *p*-ethylstyrene below 300 °C and isomerized selectively to *m*-diethylbenzene above 400 °C [5]. The structure of the active sites may change.

Table 1 lists the catalytic activity of various halide clusters for diethylamine. All of the group 5 and group 6 metal clusters became catalytically active in both the hydrogen and helium streams. The selectivities of the group 5 metal clusters differed from those of the group 6 metal clusters. The former preferentially dealkylated diethylamine to yield ethylamine and its dehydrogenation product acetonitrile in conjunction with the transalkylation product triethylamine with more than 12% selectivity, whereas the latter dehydrogenated to produce *N*-ethylideneethylamine with 61–72% selectivity. Aliphatic amines usually afford diverse products in catalysis; hence, there are few reports on selective reactions (vide infra). The activity of the clusters under hydrogen was again higher than the corresponding activity under helium. The selectivities for dehydrogenation yield-

Table 1
Dehydrogenation and disproportionation of diethylamine over various halide clusters[a]

Halide cluster	Carrier gas	Conversion[b] (%)	Selectivity[c] (%)					
			$EtNH_2$	MeCN	MeCH=NEt	EtN=CHPr	Et_3N	Others
$[(Nb_6Cl_{12})Cl_2(H_2O)_4] \cdot 4H_2O$	H_2	42.9	44.2	3.9	26.3	4.7	12.0	8.9
$(H_3O)_2[(Mo_6Cl_8)Cl_6] \cdot 6H_2O$ (**1**)	H_2	20.5	13.1	1.9	72.0	9.5	2.2	1.2
$[(Mo_6Br_8)(OH)_4(H_2O)_2]$	H_2	27.1	17.8	4.9	69.5	5.8	0.8	1.2
$[(Ta_6Cl_{12})Cl_2(H_2O)_4] \cdot 4H_2O$	H_2	30.6	33.3	10.8	30.6	4.1	14.0	7.3
$(H_3O)_2[(W_6Cl_8)Cl_6] \cdot 6H_2O$	H_2	62.4	21.3	7.5	62.4	5.6	2.6	0.8
Mo metal	H_2	4.0	33.5	5.1	45.5	13.8	2.1	0.0
–	H_2	1.3	39.8	1.0	25.0	29.7	4.5	0.0
$[(Nb_6Cl_{12})Cl_2(H_2O)_4] \cdot 4H_2O$	He	36.7	59.0	0.4	13.0	8.5	12.5	6.6
$(H_3O)_2[(Mo_6Cl_8)Cl_6] \cdot 6H_2O$ (**1**)	He	13.7	28.4	1.0	60.6	7.7	1.4	0.8
$[(Mo_6Br_8)(OH)_4(H_2O)_2]$	He	11.6	17.7	4.3	63.2	11.6	0.8	2.5
$[(Ta_6Cl_{12})Cl_2(H_2O)_4] \cdot 4H_2O$	He	10.2	55.6	0.7	19.9	6.5	15.6	1.7
$(H_3O)_2[(W_6Cl_8)Cl_6] \cdot 6H_2O$	He	4.0	36.7	1.3	38.6	14.6	4.3	4.5
$[Re_3Cl_3]Cl_3Cl_{6/2}$	He	3.2	54.1	1.3	26.6	6.9	7.8	3.3
Mo metal	He	2.4	29.6	8.2	36.6	11.0	3.8	10.8
–	He	1.2	41.8	1.5	33.9	10.5	7.6	4.6
$(H_3O)_2[(Mo_6Cl_8)Cl_6] \cdot 6H_2O$ (**1**)	N_2	26.0	18.9	3.7	67.8	7.8	0.9	0.9

[a] After treatment of the cluster (30 mg) in a stream of carrier gas (600 ml/h) at 400 °C for 1 h, reaction was started by introduction of diethylamine (0.20 ml/h, 1.9 mmol/h) at the same temperature.

[b] Conversion = products/(products + recovered diethylamine) × 100 (mol%) 3 h after reaction started.

[c] Selectivity = product/(total amount of products) × 100 (mol%) 3 h after reaction started.

Table 2
Dehydrogenation of cyclic amines over $(H_3O)_2[(Mo_6Cl_8)Cl_6] \cdot 6H_2O$ (**1**)[a]

Substrate	Carrier gas	Conversion[b] (%)	Selectivity[c] (%)				
			1-Pyrroline	Pyrrole	2,3,4,5-Tetrahydropyridine	Pyridine	Others
Pyrrolidine	H_2	21.0	83.1	13.1			3.8
	He	13.6	77.8	18.8			3.4
Piperidine	H_2	8.0			91.0	4.0	5.0
	He	6.2			80.8	6.2	13.0

[a] Reactions were performed using 1.9 mmol/h substrate at 400 °C. The other conditions are the same as given in Table 1.

[b] Conversion = products/(products + recovered amine) × 100 (mol%) 3 h after reaction started.

[c] Selectivity = product/(total amount of products) × 100 (mol%) 3 h after reaction started.

ing *N*-ethylideneethylamine and acetonitrile were somewhat higher in hydrogen than in helium, as in the case of **1**.

3.2. Reactivity of cyclic amines

Table 2 lists the catalytic activity and selectivity of **1** for cyclic amines. Pyrrolidine was dehydrogenated to the corresponding imine, 1-pyrroline, with more than 78% selectivity. Similarly, piperidine was dehydrogenated to the corresponding imine, 2,3,4,5-tetrahydropyridine, with selectivity not lower than 81%. In both cases the selectivities for the exhaustive dehydrogenation products, pyrrole and pyridine, were low. Thus, cluster **1** selectively monodehydrogenated the cyclic amines to the corresponding imines. Several stoichiometric monodehydrogenations but only a few successful catalytic methods have been reported: dioxygen oxidation of pyrrolidine to 1-pyrroline, catalyzed by a binuclear copper(II) complex in a DMF solution at ambient temperature with a turnover number of 3.12 [35], and vapor phase dehydrogenation of pyrrolidine at 200 °C over Pd/C to give 1-pyrroline with 8% yield without yielding pyrrole. However, in the latter case, when the highest yield of 1-pyrroline (24% yield) was attained at 400 °C, pyrrole formation (53% yield) dominated [36]. There are many reports on and patents for the platinum-group metal catalysts, on which complete dehydrogenation yields pyrrole or pyridine. For example, Rh/Al_2O_3 selectively converts pyrrolidine to pyrrole [37]. Solid acids have also been used in these reactions. Application of Al_2O_3 to piperidine yields pyridine with an appreciable amount of deaminated C_{10} hydrocarbon [38]. Another report on SiO_2–Al_2O_3 and Al_2O_3 catalysts describes the nonselective formation of various products, including pyridine [39]. Denitrogenation catalysts in a hydrogen atmosphere have been applied to cyclic amines as models of nitrogen-containing compounds; for the most part both denitrogenation and complete dehydrogenation occurred. Piperidine is selectively converted to *N*-pentylpiperidine by an S_{N2}-type reaction of two piperidine molecules over CoO–MoO_3/Al_2O_3 [40]. The conversion of piperidine to pyridine (48%) over Ni/NiCrO has been reported [41]. In a hydrogen stream containing H_2S, $NiMo/Al_2O_3$ catalyzes dehydrogenation of 2-methylpiperidine to 2-methyl-3,4,5,6-

Table 3
Reaction of primary and secondary amines over $(H_3O)_2[(Mo_6Cl_8)Cl_6] \cdot 6H_2O$ (**1**)[a]

Substrate	Carrier gas	Conversion[b] (%)	Selectivity[c] (%)									Deamination[d] (%)
			$EtNH_2$	MeCN	$BuNH_2$	PrCN	MeCH=NEt	PrCH=NBu	EtN=CHPr	Et_3N	Others	
Ethylamine	H_2	11.0	–	50.3			46.9				2.8	2.5[e]
	He	4.7	–	30.8			64.1				5.1	3.4[e]
Butylamine	H_2	34.7			–	90.6		5.2			4.2	4.1[f]
	He	15.6			–	79.8		12.9			7.3	3.0[f]
Diethylamine	H_2	20.5	13.1	1.9			72.0		9.5	2.2	1.2	1.8[e]
	He	13.7	28.4	1.0			60.6		7.7	1.4	0.8	3.3[e]
Dibutylamine	H_2	49.6			29.9	3.6		65.2			1.3	2.1[f]
	He	13.3			52.6	2.9		40.0			4.5	6.4[f]

[a] Reactions were performed using 1.9 mmol/h substrate at 400 °C. The other conditions are the same as given in Table 1.
[b] Conversion = products/(products + recovered amine) 3 h after reaction started.
[c] Selectivity = product/(total amount of products) × 100 (mol%) 3 h after reaction started.
[d] Mole ratio of hydrocarbons to reacted amine (mol%) 3 h after reaction started.
[e] Ethylene with small amounts of methane and ethane was formed.
[f] 1-Butene and *cis*- and *trans*-2-butene were formed in almost equal amounts.

tetrahydropyridine with 64% selectivity. The reactivity of piperidine, however, is very low [42]. Thus, selective monodehydrogenation of cyclic amines is catalytically difficult and is not achieved over these catalysts. Cluster **1**, however, proved to be a unique selective dehydrogenation catalyst in the reaction. Both the reactivities and selectivities were higher in a hydrogen stream than in a helium stream.

3.3. *Reactivity of aliphatic amines*

Table 3 lists the catalytic activity of **1** for some amines. Ethylamine was exclusively converted to acetonitrile and *N*-ethylideneethylamine. The latter, a Schiff base, would be produced by condensation of ethylamine with ethylideneamine, which is a dehydrogenation intermediate to acetonitrile [Eq. (1)] [43] but was not observed in the system.

$$EtNH_2 + MeCH{=}NH \rightarrow MeCH{=}NEt + NH_3 \qquad (1)$$

Butylamine gave the dehydrogenation product butyronitrile with more than 80% selectivity and with a small amount of the condensation product *N*-butylidenebutylamine. Deamination of ethylamine and butylamine to yield ethylene and 1-butene was negligible, with maximum contributions of the reacted amines of 4% (Table 3). Thus, cluster **1** selectively catalyzed dehydrogenation of primary amines to give the corresponding nitriles with their condensation products, Schiff bases.

Many catalysts have been applied to aliphatic primary amines. Basic metal oxides, ZrO_2 and MgO, selectively dehydrogenate primary amines to yield the corresponding nitriles [44]. Solid acids exhibit various activities: Al_2O_3 catalyzes transalkylation, dehydrogenation, condensation, and deamination of butylamine to give, nonselectively, dibutylamine, butyronitrile, *N*-butylidenebutylamine, and butenes [45,46]. Another report states that Al_2O_3 deaminates ethylamine [47] and various aliphatic primary amines [43] to give olefins with ammonia. In addition, H–MFI and Ga–MFI zeolites catalyze transalkylation of propylamine to provide dipropylamine. In–MFI further catalyzes dehydrogenation to give dipropylamine and *N*-propylidenepropylamine. Cu–MFI catalyzes C–C coupling of the alkyl substituents of propylamine and dehydrogenation to yield 2-methylpentanenitrile and propiononitrile as the major products [17,48]. These cation-exchanged MFI zeolites have Lewis acid sites. The first step on the halide cluster catalyst **1** for primary amines is dehydrogenation, which is similar to that on the basic metal oxides. However, cluster **1** catalyzed successive condensation to give *N*-alkylidenealkylamine.

The secondary amines, diethylamine and dibutylamine, selectively gave dehydrogenation products (imines) in a hydrogen stream over **1**, although dealkylation proceeded in a helium stream (Table 3). Several catalytic reactions of aliphatic secondary amines have been reported. Dibutylamine is dehydrogenated to *N*-butylidenebutylamine with 72% yield by the dihydridoiridium complex $IrH_2(\eta^3\text{-}2,6\text{-}(t\text{-}Bu_2PCH_2)_2C_6H_3)$, in the presence of 3,3-dimethyl-1-butene as a hydrogen acceptor in toluene, at 200 °C for 72 h with a turnover number of 5 [20]. Diethylamine is dehydrogenated to *N*-ethylideneethylamine with 53–76% selectivity at 350 °C in a nitrogen stream over Mo-heteropoly acid [21]. Only these two catalysts selectively produce the corresponding imines. Solid acid Al_2O_3 nonselectively catalyzes dealkylation and dehydrogenation of dibutylamine, yielding butylamine, butene, butyronitrile, and *N*-butylidenebutylamine [45]. In the case of diethylamine, disproportionation and dealkylation proceed over Al_2O_3 to give triethylamine, ethylamine, and ethane [47]. In another report, Al_2O_3 catalyzes the elimination of diisopropylamine to give propylene and isopropylamine [49]. W-heteropoly acid with a strong Brønsted acid site nonselectively catalyzes dealkylation and dehydrogenation of diethylamine to yield ethylamine, ethylene, and *N*-ethylideneethylamine [21]. Another report mentions that silica–alumina dealkylates diethylamine to ethylamine and ethylene and that acid–base bifunctional catalysts, such as SiO_2–Al_2O_3/MgO and ZrO_2, selectively transform diethylamine into acetonitrile [44]. Alicyclic amines, such as pyrrolidine and piperidine, are completely dehydrogenated over platinum-group metal catalysts, as mentioned above. However, to the best of our knowledge, the successful application of these metal catalysts to give normal dialkylimines has not been reported. It is assumed that selective dehydrogenation was unsuccessful on these catalysts. Thus, dehydrogenation selectivity of the cluster catalyst for secondary aliphatic amines, yielding the corresponding imine, differs from that of conventional acid or base catalysts but is similar to that of the Mo-heteropoly acid, which is characterized by very weak basicity, great softness, and a large polyhedral anion structure [50].

Figs. 1 and 3 and Tables 1 and 3 show that the reaction products of diethylamine always showed around 10% selectivity for N-butylideneethylamine, the butylidene group of which can be produced by C–C coupling of the ethyl substituents. The formation of butyronitrile from diethylamine over Pt–C and Pd–C catalysts has been reported, in which the formation of a five-membered cyclic amine, pyrrolidine, followed by hydrogenolysis to butylamine and dehydrogenation to butyronitrile, is assumed [51]. Production of pyrrolidine and pyrrole from diethylamine is confirmed on a Zn–Cr–Al catalyst [52]. Similarly, generation of 2-methylpentanenitrile from dipropylamine or propylamine over cation-containing MFI zeolites has been reported. Its maximum selectivity is 50% at the initial stage of the reaction [17,48]. Formation of a six-membered cyclic amine, 2-methylpiperidine, as an intermediate would result in the production of the nitrile. Formation of a small amount of butyronitrile from triethylamine over SiO_2–Al_2O_3/MgO has also been reported [44]. Taking into account such a five-membered cyclic amine as an intermediate species from diethylamine to butylamine, we can see that N-butylideneethylamine would be produced by condensation of butylideneamine with ethylamine:

$$\mathrm{HNEt_2} \xrightarrow{-\mathrm{H_2}} \mathrm{HN(CH_2)_4} \xrightarrow{\mathrm{H_2}} \mathrm{H_2NBu} \xrightarrow{-\mathrm{H_2}} \mathrm{HN{=}CHPr} \xrightarrow{\mathrm{EtNH_2},\,-\mathrm{NH_3}} \mathrm{EtN{=}CHPr}. \tag{2}$$

In the case of triethylamine, the reactivity was lower than that of the corresponding secondary amine, diethylamine, presumably because of the steric hindrance and the absence of a nitrogen-bonded hydrogen [49] (Table 4). Dealkylation and successive dehydrogenation yielded diethylamine and N-ethylideneethylamine as the major products; 54% selectivity for the former was achieved under hydrogen. This value may not be high; however, the combined selectivity for monodealkylation and the following dehydrogenation amount to 68% in a hydrogen stream and 55% in a helium stream. Dehydrogenation occurred in the alkyl chain, yielding N-vinyldiethylamine with 21–26% selectivity. Furthermore, tripropylamine and tributylamine gave the corresponding N-vinylamines as the main products in a hydrogen stream (Table 4). The elimination of a β-hydrogen is common in the formation of N-butylideneethylamine from diethylamine. There are only a few examples of the catalytic dealkylation or dehydrogenation of aliphatic tertiary amines. Only the dihydridoiridium complex has been reported to convert triethylamine into N-vinyldiethylamine (65% yield) by hydrogen transfer to 3,3-dimethyl-1-butene in p-xylene solution at 90 °C for 24 h with a turnover number of 6.5 [22]. When the acid catalyst SiO_2–Al_2O_3 is applied to triethylamine, dealkylation proceeds nonselectively, yielding diethylamine, ethylamine, and finally ethane [44]. Another report describes the formation of diethylamine with ethylene over Al_2O_3 [49]; however, the selectivity for the product is unclear. The base catalyst MgO dealkylates and dehydrogenates triethylamine to nonselectively give diethylamine, ethylamine, and acetonitrile, whereas the acid–base bifunctional catalyst silica–alumina/MgO selectively converts triethylamine to acetonitrile [44]. Consequently, selective dealkylation of trialkylamine to dialkylamine has not yet been achieved. Furthermore, the formation of even a trace amount of N-vinyldialkylamine over solid catalysts has not been reported.

3.4. Characterization of the activated cluster

The XRD pattern of **1** treated at various temperatures in a helium stream for 1 h and that of **1** subjected to a 3-h reaction at 400 °C were measured, with that of the $[Mo_6Cl_8]Cl_2Cl_{4/2}$ (Mo_6Cl_{12}, **2**) sample being synthesized independently. The samples treated at room temperature and 100 °C were assigned to $[(Mo_6Cl_8)Cl_4(H_2O)_2]\cdot 6H_2O$ (**3**) [53] and $[(Mo_6Cl_8)Cl_4(H_2O)_2]$ (**4**) [54,55], respectively. The cluster changed from **1** via **3** and **4** to the extended Mo–Cl–Mo-bonded solid state cluster **2** when heated to a temperature above 250 °C:

$$(\mathrm{H_3O})_2\big[(\mathrm{Mo_6Cl_8})\mathrm{Cl_6}\big]\cdot 6\mathrm{H_2O}\ (\mathbf{1}) \xrightarrow{\text{r.t.}} \big[(\mathrm{Mo_6Cl_8})\mathrm{Cl_4}(\mathrm{H_2O})_2\big]\cdot 6\mathrm{H_2O}\ (\mathbf{3}) + 2\mathrm{HCl} + 2\mathrm{H_2O}; \tag{3}$$

$$\big[(\mathrm{Mo_6Cl_8})\mathrm{Cl_4}(\mathrm{H_2O})_2\big]\cdot 6\mathrm{H_2O}\ (\mathbf{3}) \xrightarrow{100\,^\circ\mathrm{C}} \big[(\mathrm{Mo_6Cl_8})\mathrm{Cl_4}(\mathrm{H_2O})_2\big]\ (\mathbf{4}) + 6\mathrm{H_2O}; \tag{4}$$

$$\big[(\mathrm{Mo_6Cl_8})\mathrm{Cl_4}(\mathrm{H_2O})_2\big]\ (\mathbf{4}) \xrightarrow{250\,^\circ\mathrm{C}} [\mathrm{Mo_6Cl_8}]\mathrm{Cl_2Cl_{4/2}}\ (\mathbf{2}) + 2\mathrm{H_2O}. \tag{5}$$

The same trends were shown by Raman spectrometry. Four assigned Raman peaks (A_{1g} Mo–Cl, T_{2g} Mo–Cl, E_g Mo–Cl, and T_{2g} Mo–Mo) [56] were retained up to 100 °C. Above 250 °C, the Raman peak originally at 321 cm^{-1} and ascribed to the triply bridged Mo–Cl bending mode (A_{1g} Mo–Cl) was replaced by two peaks, suggesting a change in the coordination mode; a new peak appeared at 278 cm^{-1}. At this temperature the catalyst was active. On the other

Table 4
Reaction of tertiary amines over $(H_3O)_2[(Mo_6Cl_8)Cl_6] \cdot 6H_2O$ (**1**)[a]

Substrate	Carrier gas	Conversion[b] (%)	Selectivity[c] (%)					
			RNH_2	$R'CN$	R_2NH	$RN{=}CHR$	$R_2NCH{=}CHR''$	Others
Triethylamine	H_2	11.9	7.0	2.6	53.8	14.2	20.9	1.5
	He	2.8	15.5	0.6	19.5	35.1	26.0	3.3
Tripropylamine	H_2	16.5	6.0	3.8	23.7	11.5	51.6	3.4
	He	2.0	4.0	2.0	20.8	36.0	30.8	6.4
Tributylamine	H_2	38.8	5.6	3.5	23.1	17.5	45.0	5.3
	He	13.8	9.4	2.3	29.0	42.9	16.4	0.0

[a] Reactions were performed using 1.9 mmol/h substrate at 400 °C. The other conditions are the same as given in Table 1.

[b] Conversion = products/(products + recovered amine) 3 h after reaction started.

[c] Selectivity = product/(total amount of products) × 100 (mol%) 3 h after reaction started. $R = Et$, $R' = Me$, $R'' = H$ for Et_3N; $R = Pr$, $R' = Et$, $R'' = Me$ for Pr_3N; $R = Bu$, $R' = Pr$, $R'' = Et$ for Bu_3N.

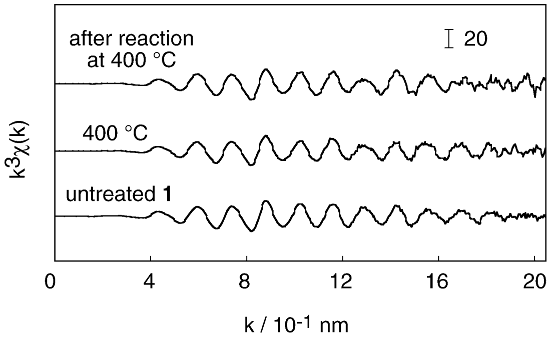

Fig. 4. k^3-Weighted EXAFS oscillations ($k^3\chi(k)$) of $(H_3O)_2[(Mo_6Cl_8)Cl_6] \cdot 6H_2O$ (**1**) treated at 400 °C with He for 1 h. The EXAFS functions of **1** subjected to 3 h reaction with diethylamine at 400 °C is also shown.

hand, the other peaks were retained above 400 °C. There was no appreciable change in the XRD patterns and the Raman spectra after a 3-h reaction with diethylamine at the same temperature, indicating that the structure of the cluster did not change during the reaction. Similar XRD patterns and Raman spectra were obtained after treatment of **1** in a hydrogen stream [5].

Fig. 4 shows the k^3-weighted EXAFS oscillations of **1** treated at 400 °C and that subjected to a 3-h reaction. These oscillations are very similar, and there were practically no changes after the catalytic reaction. The distance and the coordination number (CN) for Mo–Mo were 0.261 ± 0.002 nm and 4.2 ± 0.4, respectively, after the reaction. This CN of the Mo–Mo bond, corresponding to the octahedral metal framework, indicates the retention of the cluster framework through the reaction. The analyses of the sample treated at 400 °C in a helium stream revealed that it consisted of Mo (57.6 wt%) and Cl (40.5 wt%); the rest was only 1.9 wt%. Assuming the remainder was oxygen, the empirical formula is $Mo_6Cl_{11.4}O_{1.2}$; hence, the oxygen content was ignored for EXAFS analysis. The CN of the Mo–Cl bond of this sample was 4.4 ± 0.6; hence, the Mo–Cl bond was also retained throughout the treatment. These results clearly show the retention of the Mo cluster framework and face capping Cl ligands during the treatment and the catalytic reaction.

The dark brown sample of **1**, treated at 400 °C, and that obtained after a 3-h reaction with diethylamine in a hydrogen stream were washed with methanol, containing the recovered **1**, as $[(Mo_6Cl_8)Cl_4(OCH_3)_2]^{2+}$ (**5**) [57]. Determination of the solutions by UV spectrometry (307 nm, ε 3550 in methanol) revealed that **1** was recovered as **5** in a 92% and 87% yield, respectively. Acidification of the solutions with hydrochloric acid gave crystalline **1** in 89% and 86% isolated yields. We synthesized $[Mo_6Br_8]Br_2Br_{4/2}$ (Mo_6Br_{12}) by heating **2** in the presence of an excess of LiBr at 650–700 °C under vacuum for 1.5 h [25]. Treatment of an alkaline solution of **2** with concentrated hydrobromic acid at room temperature gives $(H_3O)_2[(Mo_6Cl_8)Br_6] \cdot 6H_2O$ [25]. Thus, the $\{Mo_6Cl_8\}^{4+}$ core is much more thermodynamically stable than the Mo–Cl bond of the terminal ligand.

The Raman spectrum and EXAFS oscillation of **1**, treated above 250 °C, were almost the same as the corresponding spectra of the solid-state cluster **2**. However, closer examination of the XRD patterns revealed that the crystallinity of **1**, treated above 250 °C, was low. Elemental analyses of **1** treated at 400 °C in helium showed a residue (1.9 wt%) originating from the coordinated water, as mentioned above. The synthesis of **2** from **1** is performed by gradual heating to 200 °C (> 2 h) followed by prolonged heating at this temperature (> 6 h) under vacuum. The coordinated water is removed by this treatment and is replaced by intercluster-bridging Cl ligands. Rapid heating to higher temperatures would give rise to the formation of imperfect crystals containing defective $[Mo_6Cl_8]Cl_2Cl_{4/2}$ moieties.

When the clusters were heated in a helium or hydrogen stream, evolution of HCl gas commenced; however, evolution of Cl_2 gas was not detected during the treatment. In the case of **1**, evolution of HCl gas continued above 250 °C, contrary to Eq. (5). The IR analyses of adsorbed pyridine on the activated $(H_3O)_2[(W_6Cl_8)Cl_6] \cdot 6H_2O/SiO_2$ shows the presence of a Brønsted acid site but not of a Lewis acid site [58]. Based on these findings and considering the electronegativity of the metals, we deduced that the terminal halogen ligand of **4** reacted with the coordinated water, eliminating HCl to give hydroxo species such as $[(Mo_6Cl_8)Cl_3(OH)(H_2O)]$ when the cluster was treated above 250 °C (Eq. (6)). The dehydrogenation and dealkylation would be catalyzed by this acidic species (Eq. (7)). Thus, small amounts of the foreign hydroxo cluster, which releases its proton, were kept in the crystal lattice of $\{[Mo_6Cl_8]Cl_2Cl_{4/2}\}_n$ above 250 °C.

$$[(Mo_6Cl_8)Cl_4(H_2O)_2]\ (\mathbf{4}) \rightarrow [(Mo_6Cl_8)Cl_3(OH)(H_2O)] + HCl, \qquad (6)$$

$$[(Mo_6Cl_8)Cl_3(OH)(H_2O)] \rightarrow H^+ + [(Mo_6Cl_8)Cl_3(O)(H_2O)]^- \qquad (7)$$

3.5. Comparison with other catalysts

Although a number of reports have been published on the catalysis and the stoichiometry of the dehydrogenation of activated amines, examples of catalytic dehydrogenation of aliphatic amines are scarce. A survey of the reports suggests that the catalysts are classified into several groups. Solid acid–base catalysts such as Al_2O_3 and SiO_2–Al_2O_3 nonselectively catalyze transalkylation, dehydrogenation, condensation, and deamination of primary, secondary, and tertiary amines [39,43,46,47,49]. Similarly, the Lewis acids, Ga–, In–, and Cu–MFI, catalyze these reactions for primary and secondary amines without selectivity [17]. H–MFI, a Brønsted acid, catalyzes transalkylation and deamination of propylamine but not dehydrogenation [17,48]. MgO, a typical solid base, selectively catalyzes dehydrogenation of primary amines to give the corresponding nitrile; however, the product selectivity of secondary and tertiary amines is low, yielding various products [59]. Consequently, the selectivity of these conventional solid acid–base catalysts differs from that of the halide cluster catalysts.

One of the proposed mechanisms for the development of an active site on the clusters is that halogen or aqua ligands of the halide cluster complexes are removed to give coordinatively unsaturated or, more likely, hydrido ligand-coordinated Mo or W metal atoms, which behave like the platinum group metals by accepting two or more electrons from the ligands [5,8]. There are many reports on group 8–10 transition metals for the exhaustive dehydrogenation of alicyclic amines [36,37,41]. However, no reports of success with *n*-alkyl amines have been published, presumably because of their high activity, leading to polyunsaturated alkyl chains or their random cleavage. In contrast, the halide cluster catalysts exhibited selective monodehydrogenation of both alicyclic and *n*-alkyl amines. Hence, these characteristic features of the halide clusters cannot be attributed to their similarity to the platinum group metals.

Molten Zn metal selectively dehydrogenates butylamine to butyronitrile, and molten Ga catalyzes the dehydrogenation followed by condensation and hydrogenation, yielding butyronitrile, butylidenebutylamine, and dibutylamine [16]; however, no other data on secondary or tertiary amines are available for comparison. There are fewer cases of dehydrogenation of amines over heteropoly acids: 12-tungstophosphoric acid catalyzes the dealkylation of diethylamine to ethylamine, but 12-molybdophosphoric acid catalyzes the selective dehydrogenation to yield *N*-ethylideneethylamine [21]. The latter's selectivity is similar to that of the halide cluster catalysts. A heteropoly acid has several types of protons, one of which originates from coordinated water [60,61], as in the halide cluster. The appearance of a Brønsted acid site in 12-molybdophosphoric acid above 130 °C has been reported, but a Lewis acid site was not observed [62]. The heteropoly anions are large and, hence, have very low charge densities on their surface [63], as in the case of the large cluster anion (Eq. (7)). The anions would not participate in the reaction in either case. Consequently, the reaction proceeded by way of the protonated amines without interaction with the counter-anions. On the other hand, alumina has been classified as a solid acid. However, it has both acidic and basic sites: incompletely coordinated aluminum ions (strong Lewis acids) and oxide ions (weak Lewis bases) [64,65]. Similarly, solid bases such as MgO [66] and hematite (α-Fe_2O_3) [67] have both basic sites as oxide ions and acidic surface sites as Mg^{2+}, Fe^{3+}, and Fe–OH. All of these sites are small and have high charge densities with participation in the reactions.

Some papers describe the effect of the hydrogen atmosphere. The absence of hydrogen increases the denitrogenation rate but decreases the dehydrogenation rate of piperidines over alumina [38]. The effect of hydrogen pressure has been reported for the reaction of piperidine over an MoO_3/Al_2O_3 catalyst: cracking dominates at low hydrogen pressure, and hydrocracking at high hydrogen pressure [40]. In a hydrogen atmosphere, the Cu ion in MFI zeolite is reduced from Cu(+) to Cu(0), and the product distribution of 1-propylamine changes [17]. In addition, gas-phase hydrogen inhibits the dehydrogenation of propylamine and prevents the formation of a carbonaceous residue on the MFI zeolite [48]. In this study, the activity of the halide clusters in a hydrogen stream was higher than that in a helium stream at the same temperature; the conspicuous deactivation of **1** in a helium stream at a temperature higher than 450 °C did not occur in a hydrogen stream (Fig. 2). Tables 1, 3, and 4 show that dealkylation or disproportionation of the alkyl group predominated in a helium stream. Accordingly, hydrogen would prevent dealkylation and the deposition of coke on the active sites. Hence, the activity and selectivity of the active sites remained high. Gaseous hydrogen is involved in the hydrogenolysis of ethylbenzene of the group 6 metal halide clusters [8].

Thus, the halide cluster exhibited unprecedented selectivity for dehydrogenation and dealkylation of amines: primary amine to the corresponding nitrile, secondary amine to the imine, and tertiary amine, which has no hydrogen bonded to the nitrogen, to the corresponding secondary amine or to the *N*-vinyldialkylamine.

4. Conclusions

When the Mo halide cluster $(H_3O)_2[(Mo_6Cl_8)Cl_6]\cdot 6H_2O$ (**1**) with an octahedral metal framework was treated above 300 °C in a hydrogen or helium stream, the catalytic activity for dehydrogenation of aliphatic amines was observed. Primary amines were dehydrogenated to the corresponding nitriles, some of which condensed to the alkylidenealkylamines. Secondary aliphatic amines were dehydrogenated to the corresponding imines. Alicyclic imines were also selectively monodehydrogenated to the alicyclic imines. Tertiary amines were dealkylated to dialkylamines, which was followed by dehydrogenation to *N*-alkylidenealkylamines, or dehydrogenated to *N*-vinyldialkylamines. The selectivities were different from conventional catalysts, such as solid acid–base catalysts or the group 8–10 transition metals. Spontaneous degradation of the protonated amine at high temperature without interaction with the counter-anion would be the driving force for the reaction. The initial step of the reactions over **1** is simple: nitrogen-bonded hydrogens are removed completely to yield nitrile or imine; when there is no such hydrogen, either a neighboring hydrogen or the nitrogen-bonded alkyl group is removed. Halide clusters of Nb, Ta, and W of the same cluster framework were also active catalysts for the dehydrogenation or dealkylation of diethylamine.

References

[1] N. Prokopuk, D.F. Shriver, Adv. Inorg. Chem. 46 (1999) 1.
[2] W. Blomstrand, J. Prakt. Chem. 77 (1859) 88.
[3] S. Kamiguchi, M. Noda, Y. Miyagishi, S. Nishida, M. Kodomari, T. Chihara, J. Mol. Catal. A 195 (2003) 159.
[4] S. Kamiguchi, M. Watanabe, K. Kondo, M. Kodomari, T. Chihara, J. Mol. Catal. A 203 (2003) 153.
[5] S. Kamiguchi, K. Kondo, M. Kodomari, T. Chihara, J. Catal. 223 (2004) 54.
[6] S. Kamiguchi, T. Chihara, Catal. Lett. 85 (2003) 97.
[7] T. Chihara, S. Kamiguchi, Chem. Lett. (2002) 70.
[8] S. Kamiguchi, S. Iketani, M. Kodomari, T. Chihara, J. Cluster Sci. 15 (2004) 19.
[9] W.P. Griffith, M. Suriaatmaja, Can. J. Chem. 79 (2001) 598.
[10] A.J. Bailey, B.R. James, Chem. Commun. (1996) 2343.
[11] W.P. Griffith, B. Reddy, A.G.F. Shoair, M. Suriaatmaja, A.J.P. White, D.J. Williams, J. Chem. Soc., Dalton Trans. (1998) 2819.
[12] S. Yamazaki, Y. Yamazaki, Bull. Chem. Soc. Jpn. 63 (1990) 301.
[13] R. Tang, S.E. Diamond, N. Neary, F. Mares, J. Chem. Soc., Chem. Commun. 562 (1978).
[14] M. Schröder, W.P. Griffith, J. Chem. Soc., Chem. Commun. (1979) 58.
[15] S. Fujibayashi, K. Nakayama, M. Hamamoto, S. Sakaguchi, Y. Nishiyama, Y. Ishii, J. Mol. Catal. A 110 (1996) 105.
[16] K. Okano, Y. Saito, Y. Ogino, Bull. Chem. Soc. Jpn. 45 (1972) 69.
[17] V. Kanazirev, G.L. Price, Stud. Surf. Sci. Catal. 84 (1994) 1935.
[18] T. Yoshida, T. Okano, S. Otsuka, J. Chem. Soc., Chem. Commun. (1979) 870.
[19] F.R. Keene, Coord. Chem. Rev. 187 (1999) 121.
[20] X.-Q. Gu, W. Chen, D. Morales-Morales, C.M. Jensen, J. Mol. Catal. A 189 (2002) 119.
[21] A.-G.A. Ali, L.I. Ali, Collect. Czech. Chem. Commun. 60 (1995) 2047.
[22] X. Zhang, A. Fried, S. Knapp, A.S. Goldman, Chem. Commun. (2003) 2060.
[23] B.Q. Xu, T. Yamaguchi, K. Tanabe, Chem. Lett. (1989) 149.
[24] F.W. Koknat, J.A. Parsons, A. Vongvusharintra, Inorg. Chem. 13 (1974) 1699.
[25] P. Nannelli, B.P. Block, Inorg. Synth. 12 (1970) 170.
[26] J.C. Sheldon, J. Chem. Soc. 410 (1962).
[27] V. Kolesnichenko, L. Messerle, Inorg. Chem. 37 (1998) 3660.
[28] D.M.P. Mingos, D.J. Wales, Introduction to Cluster Chemistry, Prentice-Hall, New Jersey, 1990.
[29] F.A. Cotton, T. Hughbanks, C.E. Runyan Jr., W.A. Wojtczak, in: M.H. Chisholm (Ed.), Early Transition Metal Clusters with π-Donor Ligands, VCH, New York, 1995, p. 1.
[30] E.A. Stern, M. Newville, B. Ravel, Y. Yacoby, D. Haskel, Physica B 208 (1995) 117.
[31] M. Newville, P. Livins, Y. Yacoby, E.A. Stern, J.J. Rehr, Phys. Rev. B 47 (1993) 14126.
[32] A.L. Ankudinov, B. Ravel, J.J. Rehr, S.D. Conradson, Phys. Rev. B 58 (1998) 7565.
[33] H.G. Karge, E.P. Boldingh, Catal. Today 3 (1988) 53.
[34] A. Lisovskii, C. Aharoni, Catal. Rev. Sci. Eng. 36 (1994) 25.
[35] S. Minakata, Y. Ohshima, A. Takemiya, I. Ryu, M. Komatsu, Y. Ohshiro, Chem. Lett. (1997) 311.
[36] D.W. Fuhlhage, C.A.V. Werf, J. Am. Chem. Soc. 80 (1958) 6249.
[37] J.M. Patterson, P. Drenchko, J. Org. Chem. 24 (1959) 878.
[38] M.J. Ledoux, M. Sedrati, J. Catal. 83 (1983) 229.
[39] S. Rajagopal, T.L. Grimm, D.J. Collins, R. Miranda, J. Catal. 137 (1992) 453.
[40] J. Sonnemans, W.J. Neyens, P. Mars, J. Catal. 34 (1974) 230.
[41] H. Adkins, L.G. Lundsted, J. Am. Chem. Soc. 71 (1949) 2964.
[42] M. Egorova, Y. Zhao, P. Kukula, R. Prins, J. Catal. 206 (2002) 263.
[43] J. Sedlacek, J. Koubek, Collect. Czech. Chem. Commun. 48 (1983) 755.
[44] B.Q. Xu, T. Yamaguchi, K. Tanabe, Appl. Catal. 75 (1991) 75.
[45] W.S. Brey Jr., D.S. Cobbledick, Ind. Eng. Chem. 51 (1959) 1031.
[46] J.P. Catry, J.C. Jungers, Bull. Soc. Chim. Fr. (1964) 2317.
[47] M.F. Ebeid, J. Pasek, Collect. Czech. Chem. Commun. 35 (1970) 2166.
[48] V.I. Kanazirev, G.L. Price, K.M. Dooley, J. Catal. 148 (1994) 164.
[49] P. Hogan, J. Pasek, Collect. Czech. Chem. Commun. 38 (1973) 1513.
[50] Y. Izumi, K. Matsuo, K. Urabe, J. Mol. Catal. 18 (1983) 299.
[51] O.V. Bragin, G.K. Gur'yanova, A.L. Liberman, Ser. Khim. (1965) 1242.
[52] D. Yusupov, R.I. Israilov, A.B. Kuchkarov, R.A. Khamidullaev, Dokl. Akad. Nauk Resp. Uzbekistan (1992) 34.
[53] C. Brosset, Arkiv. Kemi, Mineral. Geol. 22A No. 11 (1946) 1.
[54] H. Schäfer, H. Plautz, H. Bauman, W. Beckmann, C. Brendel, U. Lange, H.-G. Schulz, R. Siepmann, Z. Anorg. Allg. Chem. 389 (1972) 57.
[55] L.J. Guggenberger, A.W. Sleight, Inorg. Chem. 8 (1969) 2041.
[56] J.R. Schoonover, T.C. Zietlow, D.L. Clark, J.A. Heppert, M.H. Chisholm, H.B. Gray, A.P. Sattelberger, W.H. Woodruff, Inorg. Chem. 35 (1996) 6606.
[57] N. Perchenek, A. Simon, Z. Anorg. Allg. Chem. 619 (1993) 98.
[58] S. Kamiguchi, S. Nishida, H. Kurokawa, H. Miura, T. Chihara, J. Mol. Catal. A 226 (2005) 1.
[59] B.Q. Xu, T. Yamaguchi, K. Tanabe, Chem. Lett. (1988) 281.
[60] T. Okuhara, N. Mizuno, M. Misono, Adv. Catal. 41 (1996) 113.
[61] N. Mizuno, M. Misono, Chem. Rev. 98 (1998) 199.
[62] M. Furuta, K. Sakata, M. Misono, Y. Yoneda, Chem. Lett. (1979) 31.
[63] L. Barcza, M.T. Pope, J. Phys. Chem. 79 (1975) 92.
[64] J.B. Peri, J. Phys. Chem. 69 (1965) 220.
[65] J. Koubek, J. Volf, J. Pasek, J. Catal. 38 (1975) 385.
[66] R. Sokoll, H. Hobert, J. Chem. Soc., Faraday Trans. 1 82 (1986) 1527.
[67] U. Marx, R. Sokoll, H. Hobert, J. Chem. Soc., Faraday Trans. 1 82 (1986) 2505.