

Synthetic fluorotetrasilic mica as a support for stereoselective catalysts

T. NAKAYAMA*, S. YOSHIDA*

Division of Molecular Engineering, School of Engineering, Kyoto University, Yoshida-honmachi, Kyoto 606, Japan

H. KANAI

Faculty of Living Science, Kyoto Prefectural University, Shimogamo, Kyoto 606, Japan

Synthetic fluorotetrasilic mica (TSM) is a layered compound which has exchangeable cations between layers. Cupric cations were intercalated into TSM. X-ray diffraction study indicated that layered structures remained after calcination, but the interlayer spacings decreased. The hydrogenation of dienes with copper-exchanged TSM were investigated as heterogeneous catalysts. Ar⁺ ion-beam bombardment on the copper-exchanged TSM proved that copper was intercalated into the interlayer space. The turnover frequency (TOF) of 1,3-butadiene hydrogenation over Cu/TSM was 0.57 times lower than that over Cu/Al₂O₃ which has no structural obstacles around the active site, while the TOF of 2,3-dimethyl-1,3-butadiene hydrogenation as a bulky molecule over Cu/TSM was 0.03 times lower than that over Cu/Al₂O₃. TSM possesses an advantage over conventional supports in that bulky substrates have hardly any access to catalytically active sites in the interlayer space.

1. Introduction

Synthetic fluorotetrasilic mica, a layered compound, has a similar structure to montmorillonite or hectorite. These layered compounds have exchangeable cations in the interlayer space. Not only metal cations but also cationic metal complexes can be intercalated into the interlayers. Intercalated rhodium-complex catalyst was investigated in the hydrogenation of hexynes [1]. Catalytically active species in the interlayer space of hectorite worked with special functionalities. The critical dimension of 1- or 2-hexyne is smaller than the distance between two layers, so that hydrogenation occurred at the same rate as that of the homogeneous catalyst. However, the critical dimension of 3-hexyne is larger than the interlayer spacings and the hydrogenation rate of 3-hexyne was an order of magnitude lower than that of 1- or 2-hexyne. This result indicates the hydrogenation of 3-hexyne occurred only on the top-most layer or at the mouth of the interlayer space which have fewer species. Thus layered compounds might be a kind of functional support, as are zeolites. From the materials scientific point of view, Yamanaka and Brindley [2] reported that nickel hydroxypolycation could be intercalated into montmorillonite and formed pillars in the interlayers. Intercalated Ni²⁺ and Cu²⁺ ions in montmorillonite were reduced with hydrogen at 553 K [3]. These studies on natural minerals prompted us to use synthetic layered compounds. We investigated the effectiveness of synthetic fluorotetrasilic mica as a specific support of catalysts.

2. Experimental procedure

2.1. Materials

Fluorotetrasilic mica (TSM) was supplied by Topy Industries, Ltd. It was separated to a fraction below 2 μm diameter by sedimentation. The chemical composition of TSM is Na[Mg_{2.5}Si₄O₁₀F₂]. Montmorillonite (Mont) was supplied by Kunimine Co., and used without further purification. The chemical composition of Mont is Na[Al₃Mg(Si₄O₁₀)₃(OH)₆]. Hectorite (Hect) mined at Hector, CA (API 34) was pulverized with a vibratory rod mill, separated to a fraction below 2 μm diameter by sedimentation, and used. The chemical composition of Hect is Na[Mg₈Li(Si₄O₁₀)₃(OH,F)₆]. Copper formate, Cu(HCOO)₂·4H₂O, was used as a source of intercalating cations. Dienes were used after vacuum distillation.

2.2. Preparation of metal-intercalated catalysts

The exchange method was used in this investigation. An aqueous copper formate solution (0.01–0.1 mol l⁻¹) was added to intercalation compounds (1.0 g) suspended in deionized water (100 ml) and the mixture was stirred overnight at room temperature, followed by filtering or centrifuging, and then washed several times with 300 ml water. The ion-exchanged intercalated compounds were air-dried at room temperature. The copper content was estimated by the difference between the total amount of copper cations

* Present address: Sumitomo Metal Industries, Ltd, Wakayama Steel Works, 1850 Minato, Wakayama 640, Japan.

added and that of a mixture of the filtrate and washings determined by chelate titration.

2.3. Characterization of intercalated compounds

The intercalated compounds both before and after calcination at 573 K in air were characterized by X-ray photoelectron spectroscopy (XPS) (Shimadzu ESCA-750). Utilizing a magnesium source (8 kV, 30 mA), survey spectra and multiplex spectra for C_{1s} , Cu_{2p} , Al_{2p} , Si_{2p} and O_{1s} regions were recorded. The XPS system has an Ar^+ ion gun to sputter off the surface. The ion gun was operated at 2 kV and 20 mA emission at 1×10^{-2} Pa argon pressure. The sputtering rate was determined as 5 nm min^{-1} . We also used X-ray diffraction (XRD) (Material Analysis and Characterization Inc. MXP-3) for structural characterization.

2.4. Hydrogenation of dienes catalysed by intercalated compounds

Copper catalysts were calcined in the air at 573 K prior to hydrogenation. Calcined catalysts were placed in a conventional glass-made circulating system and reduced with hydrogen (40 kPa) at 573 K for 2 h. After the reduction procedure, the system with catalysts was pumped down to 10^{-1} Pa, and diene (2.6–6.7 kPa) and hydrogen (13–40 kPa) were introduced into the system at 573 K. Products were analysed by a gas-chromatograph (Shimadzu GC-3BF) equipped with 25% dimethylsulpholane/C-22 column (5.6 m) at room temperature.

3. Results and discussion

3.1. Characterization of intercalated catalysts

It is very difficult to look into the interlayer space using surface science techniques. However, XPS with argon sputtering makes this "black box" clear. Soma *et al.* [4] investigated Na/TSM as an initial layered compound by XPS. They concluded that an exchangeable sodium cation exhibited a different binding energy from unexchangeable sodium. This result indicated that the exchanged cation has different electron density from a discrete cation. The XPS binding energy of Cu_{2p} of Cu/TSM after calcination in hydrogen at 573 K was 932.5 eV, so that the copper was reduced to metallic or monovalent (Table I), while that before calcination was determined as divalent [5]. Owing to the insulation materials, the surface was charged up within 3 V, so that the calibrated binding energies adopted in this study were based on an internal reference of the C_{1s} line, which was fixed to 285.3 eV. The different binding energies of intercalated copper indicate that the electron density is affected by silicate layers. Copper formate was used as an intercalating source because it decomposes easily with heat treatment [6]. The depth profile of Cu_{2p} binding energy of Cu/TSM using an argon beam sputtering is illustrated in Fig. 1. The peak intensity oscillates irregularly because the sputtering rate was 5 nm min^{-1} , while the

TABLE I Binding energy of $Cu_{2p_{3/2}}$ ^a

Catalyst	Binding energy (eV)	
	Before calcination	After calcination ^b
Cu/TSM	933.2	932.5
Cu/Hect	933.3	932.6
Cu/Mont	933.8	932.4
Cu/SiO ₂	933.8	932.4

^a Measured by XPS.

^b Calcination was carried out in hydrogen at 573 K.

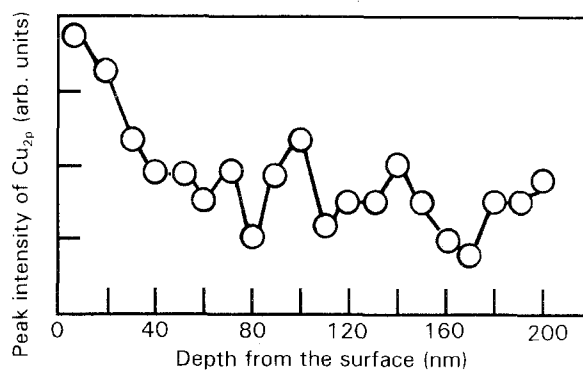


Figure 1 Depth profile of Cu_{2p} peak intensity on Cu/TSM using argon-ion sputtering (sputtering rate 5 nm min^{-1}).

thickness of the silicate layer and interlayer spacings are 0.93 and 0.12 nm, respectively. The intensity of the Cu_{2p} binding energy in the interlayer space is high, while that in the silicate layer structure is low. However, the high intensity of Cu_{2p} binding energy detected in deep layers away from the surface indicated that copper was intercalated into the interlayer space. A similar trend was observed for the XPS of Cu/Hect, while no peaks of Cu_{2p} were recorded in the deep layer of Cu/Mont. Therefore, the copper cation was not intercalated into the interlayer of montmorillonite.

Table II shows the XRD results of layered compounds. The observed 001 basal reflection (d_{001}) of the silicate layer of TSM intercalated with copper cations corresponds to a spacing of 1.05 nm. Because the thickness of the silicate layer is 0.93 nm [7, 8], the average Δd_{001} value, which is a measure of the interlayer spacings between two layers, is 0.12 nm. Copper-exchanged hectorite had a layered structure before calcination at 573 K; however, the XRD after calcination indicates the layered structure collapsed. As a reference for XRD measurements, copper cation-exchanged Y-zeolite was investigated both before and after calcination. The d -spacing and related pore size were the same value as those given by Breck [9] and no change was observed between the states before and after calcination. Pinnavaia *et al.* [1] determined that in the case of methanol-solvated $Rh(PPh_3)^+/Hect$, the Δd_{001} was 0.77 nm.

Critical dimensions of 1,3-butadiene, isoprene and 2,3-dimethyl-1,3-butadiene were estimated at 0.40, 0.50 and 0.65 nm, respectively, based on a space-filling model [10, 11]. Because the critical dimension of 1,3-butadiene is not smaller than the distance of interlayer spacings and the surface area of Cu/TSM was extremely small, the hydrogenation occurred at the

TABLE II Basal reflection, d_{001} , and interlayer spacings, Δd_{001}^a

Compound	d_{001} (nm)		Δd_{001} (nm)
	After air drying	After calcination at 573 K	After calcination at 573 K
1.8% Cu/TSM	1.24	1.05	0.12 ^b
11% Cu/Hect	1.13	Collapsed ^c	–
3.1% Cu/Mont	1.41	Collapsed ^c	–

^a Measurements by XRD.

^b Thickness of the silicate layer was 0.93 nm measured after the calcination at 773 K as the collapsed interlayer.

^c Silicate sheet thickness was observed.

TABLE III Hydrogenation of dienes on copper catalysts

Catalysts	Saturated amount of chemisorbed CO (10^{-5} mol g-cat ⁻¹)	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Initial rate of hydrogenation ^a			Turnover frequency ^b		
			$(10^{-6} \text{ mol s}^{-1} \text{ g-cat}^{-1})$			(s^{-1})		
			BD	MBD	DMBD	BD	MBD	DMBD
1.8% Cu/TSM	0.1	2.5	0.95	0.14	0.0067	95 (0.57)	14 (0.10)	0.67 (0.03)
11% Cu/Hect	0.7	–	5.0	2.5	0.98	71 (0.43)	35 (0.13)	14 (0.63)
5% Cu/Al ₂ O ₃	1.4	125	23	20	3.1	160 (1.0)	140 (1.0)	22 (1.0)

^a BD, 1,3-butadiene; MBD, isoprene; DMBD, 2,3-dimethyl-1,3-butadiene.

^b The number in parentheses is the relative turnover frequency to Cu/Al₂O₃ is 1.0.

TABLE IV Product distribution in the hydrogenation of 1,3-butadiene^a

Catalysts	Hydrogenation rate (10^{-5} mol s ⁻¹ g-Cu ⁻¹)	Products (%)			
		<i>n</i> -butane	1-butene	<i>trans</i> -2-butene	<i>cis</i> -2-butene
1.8% Cu/TSM	5.3	0.3	59.3	23.4	17.0
6.2% Cu/Hect	8.1	2.0	42.0	31.8	24.1
3.1% Cu/Mont	1.0	2.8	32.8	44.5	19.8
5% Cu/Al ₂ O ₃	45	17.1	23.8	33.6	25.4
5% Cu/SiO ₂	51	1.8	47.7	28.2	22.3

^a Hydrogenation was carried out with $p(\text{butadiene}) = 6$ kPa and $p\text{H}_2 = 17$ kPa at 573 K.

mouth of the interlayer space. However, ²⁹Si-magic angle spinning nuclear magnetic resonance (MAS-NMR) studies [12] on Ca²⁺/TSM supported the idea that the calcium cation was fixed on the hexagonal holes of the basal oxygen plane of the silicate layer in a completely random fashion. To apply these results, these hexagonal holes were opened with exchanged copper cations at the mouth of the silicate layers. So the active site was incompletely exposed to the atmosphere and the steric effect in the hydrogenation of bulky dienes such as 2,3-dimethyl-1,3-butadiene was observed.

3.2. Catalytic study

Table III shows the results of hydrogenation of conjugated dienes. 1,3-butadiene, the smallest of the three dienes, the critical dimension of which is small, is easily accessible to the catalytic active site. In the 1,3-butadiene hydrogenation, the turnover frequency (TOF) over copper-exchanged TSM was 0.57 times lower than that over Cu/Al₂O₃ which has no structural barrier around the catalytically active site. The TOF of isoprene over Cu/TSM was one-tenth of that over Cu/Al₂O₃ (Table II). Furthermore, a bulky diene

such as 2,3-dimethyl-1,3-butadiene could not access the catalytically active site of Cu/TSM, so that the rate of hydrogenation or TOF was extremely low. A small portion of the active sites on the top-most surface was only employed in the hydrogenation of 2,3-dimethyl-1,3-butadiene. Sakurai *et al.* [12] investigated Ca²⁺-intercalated TSM with aluminium hydroxy polycation to form pillars in the interlayer space after calcination, as an acidic catalyst. Intercalated calcium cation by an exchange method also formed pillar-like structures to maintain the interlayer spacings after calcination. These catalysts have acidic sites which are catalytically active for cumene cracking. However, Sakurai *et al.* did not discuss the sizing or stereocontrolling effects of layered structures. Morikawa *et al.* [13, 14] investigated dehydrogenation of methanol to methyl formate catalysed by copper-exchanged TSM. The high selectivity and activity are caused by both the non-acidity of TSM and the high resistance of the exchanged copper cation against reduction. Their results indicated that the copper in the interlayer space would not remain metallic but was transformed to ionic by silicate layers during dehydrogenation in nitrogen. However, heat treatment at 573 K in hydrogen prior to the reaction would induce the

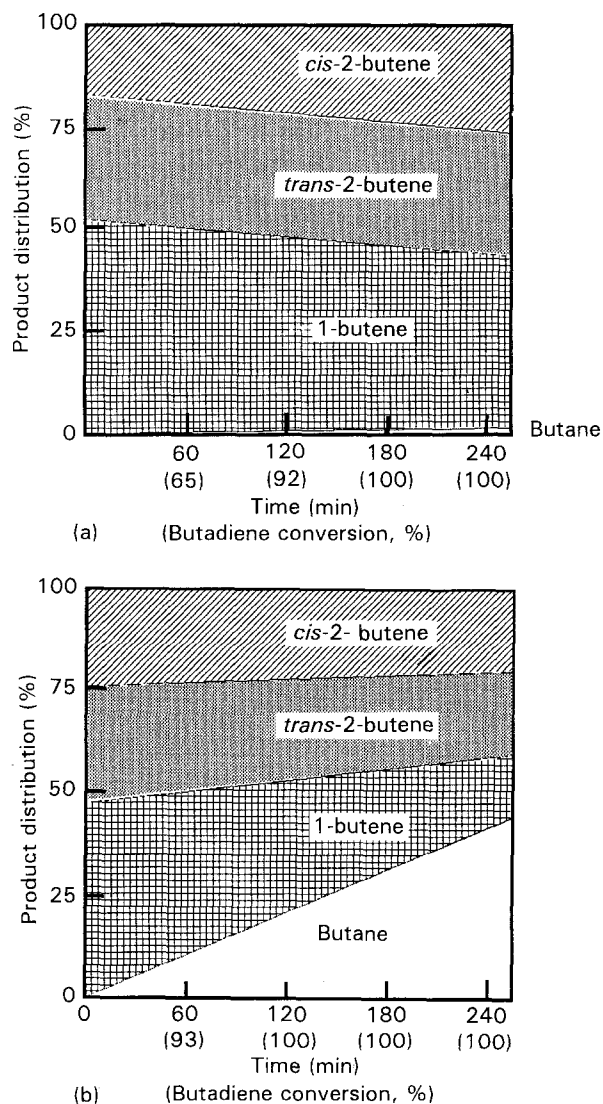


Figure 2 Time course of the product distribution in the hydrogenation of 1,3-butadiene ($p_{H_2} = 40$ kPa, $p_{C_4H_6} = 6.3$ kPa at 573 K), (a) over Cu/TSM, (b) over Cu/SiO₂.

copper in the interlayer space to be metallic or monovalent. Therefore, the product selectivity in the hydrogenation of 1,3-butadiene (Table IV) over Cu/TSM was similar to that over Cu/SiO₂, while the reaction over Cu/Mont was similar to that over Cu/Al₂O₃. Furthermore, these results might indicate that the main composition of the layered structure of TSM is silicon oxides without aluminium oxides, while that of montmorillonite is silicon oxides with aluminium oxides which has a catalytically stronger influence on metal than do silicon oxides.

After 1,3-butadiene was consumed, butenes were hydrogenated to butane over conventional supported catalysts (Cu/SiO₂, Cu/Al₂O₃); however, Cu/TSM was almost inactive for the hydrogenation of butenes. Moreover, the isomerization of butenes was inhibited (Fig. 2). These results indicate that the critical dimensions of coordinated butenes with active sites might be larger than the hexagonal hole which stereo-controls the reaction.

4. Conclusion

Fluorotetrasilic mica has an advantage as a support of the catalyst. XPS results indicated that copper cation was intercalated into the interlayer space; however, the interlayer spacings were reduced less than the critical dimension of dienes after calcination at 573 K. The BET surface area of Cu/TSM after calcination at 573 K indicates the interlayer space is too narrow for molecules to access. However, copper cations fixed on the hexagonal hole at the mouth of the silicate layers might have played a major role in controlling the size of molecules.

References

1. T. J. PINNAVAIA, R. RAYTHATHA, J. G. LEE, L. J. HALLORAN and J. F. HOFFMAN, *J. Amer. Chem. Soc.* **101** (1979) 6891.
2. S. YAMANAKA and G. W. BRINDLEY, *Clays Clay Miner.* **26** (1978) 21.
3. M. PATEL, *ibid.* **30** (1982) 398.
4. M. SOMA, A. TANAKA, H. SEYAMA, S. HAYASHI and K. HAYAMIZU, *Clay Sci.* **8** (1990) 1.
5. C. D. WAGNER, W. M. RIGGS, L. E. DAVIS, G. E. MOULDER and G. E. MUILENBERG, "Handbook of X-ray Photoelectron Spectroscopy" (Perkin-Elmer, Eden Prairie, MN, 1978).
6. H. HAYASHI, H. NISHI and T. OKAZAKI, *J. Chem. Soc. Jpn.* (1981) 1825.
7. H. SAKURAI, K. URABE and Y. IZUMI, *Bull. Chem. Soc. Jpn.* **63** (1990) 1389.
8. *Idem, ibid.* **62** (1989) 3221.
9. D. W. BRECK, "Zeolite Molecular Sieves" (Wiley, New York, 1974) p. 369.
10. C. N. SATTERFIELD and C. S. CHANG, *AIChE Symp. Ser.* **67** (1971) 43.
11. R. L. GORRING, *J. Catal.* **31** (1973) 13.
12. H. SAKURAI, K. URABE and Y. IZUMI, *Bull. Chem. Soc. Jpn.* **64** (1991) 227.
13. Y. MORIKAWA, K. TAKAGI, Y. MORO-OKA and T. IKAWA, *Chem. Lett.* (1982) 1805.
14. Y. MORIKAWA, Y. MORO-OKA and T. IKAWA, *ibid.* (1982) 1667.

Received 19 June 1992

and accepted 3 February 1993