Original

Catalytic Materials Made of Sepiolite

by

Kazuo URABE[†]

ABSTRACT

The cation exchange capacity (CEC) of sepiolite is greatly enlarged by the ion exchange in an aqueous solution at a high temperature of 95°C as well as the precalcination of original sepiolite at temperatures over 500°C. The Ni ions incorporated for Mg ions in sepiolite crystal exist in the divalent state and are octahedrally-coordinated. An original sepiolite without metal-ion exchange is completely inert as a catalyst for any reactions. However, the fixation of Ni or Zn confers higher catalytic activity on it for the dehydration of n-butyl alcohol or the benzylation of benzene, respectively.

Key Words : Sepiolite clay, Catalyst, Cation exchange capacity, Alcohol dehydration, Benzene alkylation

1. INTRODUCTION

Sepiolite belongs to the sepiolite-palygorskite clay mineral family, also known as the hormite group. Its ideal chemical formula is $(\text{Mg}_8)_{\text{oct}}(\text{Si}_{12})_{\text{tet}}\text{O}_{30}(\text{OH})_4(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$. In recent years it has attracted considerable interest owing to its wide range of applications from deodorant materials such as pet litter to catalyst carriers [1]. It is a fibrous magnesia-silicate which contains zeolitic water (depicted as ② in Fig. 1 (a)) in its one-dimensional intracrystalline channel, as illustrated in Fig. 1 (a). The magnesium (Mg) ion in sepiolite crystal is known to be exchangeable with other ions [2]. However, the applicability of sepiolite as catalytic material has been restricted [3] due to its small cation exchange capacity (CEC) of about 40 meq/100g [4,5]. The present work reports a successful attempt to enlarge CEC of sepiolite and apply it to two types of catalytic reactions.

2. EXPERIMENTAL

An original sepiolite (Aid-plus G, Mizusawa Chem. Ind.) was calcined for 4 h at various temperatures *prior to* cation exchange manipulation. Then 1.6 g of the calcined sepiolite was added to 100ml of 0.1 N metal salts (nitrate or acetate) aqueous solution and the dispersed solution was stirred at

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[†] Department of Applied Chemistry, School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

Fig. 1 Schematic structure of sepiolite; a) Regular [1] and b) *Folded* structure [1].

95°C for 24 h for cation exchange. The product was filtered, washed repeatedly with deionized water and air-dried overnight at 60°C. For comparison, some cation-exchange samples were also prepared at room temperature.

The vapor-phase catalytic reactions for dehydration of n-butyl alcohol were carried out at 200°C under hydrogen flow using a conventional flow reaction apparatus with a fixed bed of catalyst. The catalyst was reduced at 400°C for 1 h under hydrogen flow prior to dehydration reaction. On the other hand, the liquid-phase alkylation reactions of benzene were carried out at 30°C in a round-bottom flask under nitrogen atmosphere. Prior to the reaction, the catalyst was vacuum-dried under 0.5 torr at 120°C for 3 h. All reaction products were analyzed by gas chromatography.

3. RESULTS AND DISCUSSION

Enlargement of the cation exchange capacity (CEC) of sepiolite

The cation exchange experiments on sepiolite using nickel acetate solution were carried out under various conditions. The contents of Ni and Mg ions in the Ni-sepiolites were determined analytically and shown Table 1. These amounts are expressed as mol% in the table. The amount of fixed Ni is also expressed for convenience as meq/100g-clay. It is estimated to be 49 meq/100g for the sample exchanged at room temperature of uncalcined sepiolite (conventional method). This value agrees with the cation exchange capacity (CEC) of about 40 meq/100g reported commonly in the literature [4,5]. On the other hand, the exchange at a high temperature of 95°C causes fourfold increase of fixed Ni (195 meq/100g) compared to that at room temperature.

Furthermore, marked increase of fixed Ni was brought about by the calcination of original sepiolite at higher temperatures. Fig. 2 shows the amount of fixed Ni as a function of the precalcination temperature. Up to a precalcination temperature of 400°C, the amount of fixed Ni in the Ni-sepiolite, whether exchanged at 95°C or at room temperature, hardly increases. However, it increases dramatically at temperatures over 500°C. For example, 525 meq/100g of Ni was fixed for the sample exchanged at 95°C of sepiolite calcined at 700°C. This value is one order of magnitude larger

Table 1. Contents of Ni and Mg ions in the Ni-sepiolites exchanged under various conditions.

Ni-sepiolite		Contents/mol%		CEC/meq (100g) ⁻¹ for fixed Ni ^b	Surface area ^c /m ² g ⁻¹
Precalcination temperature/°C	Ni-exchange temperature/°C	of Ni ^a	of Mg ^a		
750	95	0.264	0.272	548	182
700	95	0.254	0.263	525	190
600	95	0.135	0.412	276	132
500	95	0.135	0.580	276	—
400	95	0.101	0.486	209	132
300	95	0.089	0.519	183	—
60 (dried)	95	0.094	0.502	195	150
700	r.t. ^d	0.083	0.469	173	120
600	r.t.	0.053	0.580	109	110
500	r.t.	0.032	0.638	66	—
60 (dried)	r.t.	0.027	0.601	49	—

a) Determined by the ICP spectroscopic method. b) See the text. c) B.E.T. type N₂ adsorption isotherm. d) Room temperature.

than that by the conventional exchange method. It means that 165% of constituent Mg ions (see Fig. 1 (a)) exposed to the channel space is exchanged for Ni ions. On the other hand, 173 meq/100g was fixed for the Ni-sepiolite exchanged at room temperature of sepiolite calcined at 700°C.

It can also be seen from Table 1 that the decreased amount of Mg is comparable to the fixed amount of Ni in almost all Ni-sepiolites. This means that the cation-exchange between the Mg ion in sepiolite crystal and the Ni ion in solution is a key mechanism. Thus, it seems that the great enlargement of CEC of sepiolite is brought about by both the ion exchange in an aqueous solution at a high temperature of 95°C and the precalcination of original sepiolite at temperatures over 500°C. The value of the enlarged CEC in sepiolite extends to several times that of montmorillonite (about 100 meq/100g), or a typical smectite clay.

Structure of Ni-sepiolite exchanged at high temperatures

By the calcination of original sepiolite, its specific surface area gradually decreased from about 200 m²/g at 200°C to 70 m²/g at 800°C. The extensive decrease (200 m²/g at 200°C to 130 m²/g at 300°C) that occurs by heating at about 300°C is related to the formation of well-known *folded structure* (*folding*) [4], resulting from the loss of bound water molecules in the channels (compare Fig. 1. b with Fig. 1. a). The structure of *folded* sepiolite is depicted in Fig. 1(b). However, the subsequent Ni exchange at a high temperature of 95°C brings about recovery of the surface area. Any Ni-sepiolite exchanged at 95°C holds a high value of 130-180 m²/g as shown in Table 1.

Crystallinities of sepiolite samples treated under various conditions were examined by XRD method. Uncalcined sepiolite, with or without Ni exchanging at 95°C, reveals an intense typical (110) reflection peak of about 12.2 Å. On the other hand, the precalcination of an original sepiolite at 650°C causes almost loss of peak at 12.2 Å and an appearance of weak peak at 10.4 Å instead of 12.2 Å, indicating the formation of *folded* sepiolite at this temperature [4]. However, the Ni exchange at

Fig. 2. Amount of fixed Ni as a function of the precalcination temperature of sepiolite.

Fig. 3. ²⁸Si MASNMR spectra of sepiolites treated under various conditions.

95°C does not bring about the re-appearance of the (110) reflection peak at 12.2 Å.

The chemical state of fixed Ni in Ni-sepiolite was studied by UV-Vis and XPS spectroscopy. The diffuse reflectance UV-Vis spectrum of powdered Ni-sepiolite has a strong resemblance to that of well-known $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ aqueous ions [6], indicating that the Ni in the Ni-sepiolite is divalent and octahedrally-coordinated. XPS spectrum of Ni-sepiolite gives characteristic quadruple peaks in the range of 860 to 900 eV of binding energy unit. This spectrum pattern has been assigned to divalent Ni, too.

Fig. 3 shows the ^{29}Si MASNMR spectra of sepiolites treated under various conditions. Uncalcined original sepiolite gives a symmetric triple signal [7], indicating three types of Si nucleus, as shown in Fig. 1(a). The calcination at 650°C causes the breaking of symmetry in its spectrum, evidencing the change in the chemical environment of Si nucleus by *folding* (see Fig. 1(b)). The subsequent Ni-exchange at room temperature almost never influences the spectrum. In contrast, the exchange at a high temperature of 95°C causes a substantial change in spectrum. The ^{29}Si NMR spectrum of Ni-sepiolite exchanged at 95°C is nearly identical to that of uncalcined original sepiolite, demonstrating a cancellation of *folding*, or a structural recovery of Si-O linkage in sepiolite crystal by the ion exchange at 95°C. This is in harmony with the result of recovery of surface area by the ion exchange at 95°C described above.

From these results, it is concluded that the fixation of Ni does not destroy the sepiolite structure in substance and the divalent Ni ions constitute a part of the structure for Mg ions. Moreover, the precalcination of original sepiolite at temperatures over 500°C causes a lattice deformation (*folding*) round the Mg ions exposed to the channel space to enhance a cation-exchange of the Mg ion in the lattice with the Ni ion in solution at 95°C. Detailed structural data were shown elsewhere [8].

Table 2. Contents of M^{n+} ions and Mg ions in M^{n+} -exchanged sepiolites.

M^{n+} -sepiolite		Contents ^a /mol%		CEC ^b /meq (100g) ⁻¹ for fixed M^{n+}	Ionic radius of ion/Å
Sort of exchanged ion	M^{n+} -exchange temperature/°C	of M^{n+}	of Mg		
Mn	r.t. ^c	0.020	0.621	40	0.70
Mn	95	0.087	0.547	176	0.70
Cu	r.t.	0.027	0.617	54	0.72
Cu	95	0.050	0.564	99	0.72
Ni	r.t.	0.027	0.601	49	0.83
Ni	95	0.094	0.502	195	0.83
Zn	r.t.	0.026	0.617	52	0.88
Zn	95	0.046	0.568	92	0.88
Ca	r.t.	0.005	0.527	12	1.06
Ca	95	0.007	0.531	16	1.06
Ba	r.t.	0.001	0.461	3	1.43
Ba	95	0.002	0.465	4	1.43

a) Determined by the ICP spectroscopic method. b) See the text. c) Room temperature.

Kind of exchangeable cation for Mg ion in sepiolite

By employing various cations other than Ni, the Mg ions in sepiolite crystal were exchanged as shown in Table 2. For these experiments, uncalcined sepiolites were used. The amount of fixed Zn, Mn, or Cu at room temperature is 40-50 meq/100g, or very similar to that of Ni. The exchange at 95°C also causes 2-4 times increase of fixation amount for these cations. It is noticeable that these cations have similar ionic radius to that of Mg (0.86 Å), or Zn (0.88), Ni (0.83), Cu (0.72), Mn (0.70). In contrast, for Ca (1.06) or Ba (1.43) with much larger radius than Mg, the incorporation of cation into sepiolite were hardly observed. Further, the exchange at 95°C does not affect at all for Ca or Ba. These facts strongly suggest that the size of cation is of central importance in the cation-exchange phenomena of sepiolite. In other words, a kind of 'size-memory effect' works in this system.

Application of metal-exchanged sepiolite to catalytic reactions

An original sepiolite without cation-exchange procedure, in itself, is completely inert as a catalyst for any reactions despite its large surface area. The incorporated metal-ions by cation-exchange confer catalytic functions on sepiolite. Two examples are taken here by Ni- and Zn-exchanged sepiolite.

Firstly, Ni-exchanged sepiolite works as an excellent catalyst for the selective intermolecular dehydration of *n*-butyl alcohol to dibutyl ether as shown in Eq.1.

This reaction is novel and peculiar to low-valent Ni catalyst for petrochemical uses [9]. Table 3 illustrates the catalytic efficiencies for this reaction of Ni-exchanged sepiolites prepared under various exchange conditions. The Ni-exchanged sepiolite (Ni content = 49 meq/100g) at room temperature (conventional method) manages only a 5% yield of dibutyl ether at 200°C and WHSV = 1 h⁻¹. In con-

Table 3. Catalytic efficiencies of the Ni-sepiolites prepared under various conditions for the dehydration of *n*-butyl alcohol^a.

Ni-sepiolite		Contents of Ni ^b /mol%	Catalytic efficiencies	
Precalcination temperature/°C	Ni-exchange temperature/°C		Yield of ether ^c /%	Selectivity for ether/%
700	95	0.254 (525) ^d	28	47
650	95	0.147 (292)	30	47
600	95	0.135 (276)	26	46
400	95	0.101 (209)	21	69
60 (dried)	95	0.094 (195)	28	66
60 (dried)	r.t. ^e	0.027 (49)	5.3	71
Original sepiolite without Ni		0	trace	—

a) Reaction temp. = 200°C, WHSV = 1.0 h⁻¹, flow rate of H₂ carrier gas = 1000 ml/h, averaged initial efficiency for 1 h after feeding of reactant. b) Determined by the ICP spectroscopic method. c) Dibutyl ether. d) Figure in parentheses denotes the content of Ni expressed as CEC equivalent (see Table 1 and the text). e) Room temperature.

trast, the sample exchanged at 95°C of sepiolite calcined at 600°C (Ni content = 276 meq/100g) displays a high catalytic activity, with a dibutyl ether yield of 26%, five times as much as the sample exchanged at room temperature. The Ni content of 276 meq/100g corresponds to an exchange rate of 85% in constituent Mg ions exposed to the channel space.

The dependence of dibutyl ether yield given by various Ni-exchanged sepiolites upon Ni content of each catalyst was examined in detail [8]. The yield of dibutyl ether as a catalytic efficiency increases linearly with a rise in Ni content, coming to a saturated value at a Ni content of more than 0.1 mol%. Interestingly, the Ni content causing this saturation of catalytic efficiency is nearly equal to the exchange rate of 100% in exposed Mg ions, suggesting that excess Ni ions incorporated into bulk do not work as effective catalytic sites for the conversion of n-butyl alcohol. It is concluded that the Ni incorporated into sepiolite crystal plays not only a crucial role as a catalyst but also that the number of Ni ions situated on proper sites regulates the catalytic efficiency of dehydration reaction.

Second example is Zn-exchanged sepiolite, which works as an efficient solid Friedel-Crafts alkylation catalyst for liquid-phase use. The tested alkylation reaction is benzylation of benzene by benzyl chloride as shown in Eq.2.

In other word, this catalyst is regarded as one of 'environmentally friendly catalysts' [10] because it can reduce the problems, such as corrosion and water pollution, associated with the conventional Friedel-Crafts reaction using homogeneous $AlCl_3$ catalyst. Table 4 shows the catalytic efficiencies of Zn-sepiolites prepared under various exchange conditions. The Zn-sepiolite exchanged at room temperature (conventional method) manages only a 2.3% yield of diphenyl methane at 30°C. In contrast, Zn-sepiolite exchanged at 95°C of sepiolite calcined at 700°C (Zn content = 504 meq/100g) exhibits a highest catalytic activity, with a diphenyl methane yield of 20%, nine times as much as the sample ex-

Table 4. Catalytic efficiencies of the Zn-sepiolites prepared under various conditions for the benzylation of benzene^a.

Zn-sepiolite		Contents of Zn ^b /mol%	Catalytic efficiencies	
Precalcination temperature/°C	Zn-exchange temperature/°C		Conversion of benzyl chloride/%	Yield of diphenylmethane/%
700	95	0.252 (504) ^c	39	20
700	r.t. ^d	0.052 (104)	16	2.5
60 (dried)	95	0.046 (92)	27	19
60 (dried)	r.t.	0.026 (52)	2.3	2.3
Original sepiolite without Zn		0	0	0
Zn ²⁺ -montmorillonite		0.055 (118)	40	23

a) Reaction temp.=30°C, benzyl chloride=5 mmol, benzene=100 mmol, catalyst=63mg, benzyl chloride/cat. (w/w)=10, 2 h after starting the reaction. b) Determined by the ICP spectroscopic method. c) Figure in parentheses denotes the content of Zn expressed as CEC equivalent (see Table 1 and the text). d) Room temperature.

changed at room temperature. This high efficiency is compared to that of a recent-popular Zn^{2+} -montmorillonite catalyst (trade name; *envirocat*) [10] as shown in the last line of Table 4. Zn-sepiolite exchanged at 95°C of uncalcined sepiolite also shows a comparable high efficiency (19%) to the Zn-sepiolite exchanged at 95°C of sepiolite calcined at 700°C despite its much lower Zn content of 92meq/100g. It seems that Zn-exchange procedure at 95°C is quite important, whether with or without calcinating an original sepiolite at 700°C, in order to make an active Friedel-Crafts catalyst.

It is noticeable that Zn-exchanged one exhibits a highest activity among various cation-exchanged sepiolites. Ni-, Fe-, or Al-exchanged sepiolite manages a yield of less than 2% even when prepared through exchanging at 95°C of uncalcined sepiolite. This element-specificity lead us to a new finding that Zn-bearing fraipontite clay was more active for this reaction than Zn^{2+} -montmorillonite [11]. Fraipontite is a synthetic 1:1 type clay like kaolinite with a structural formula of $(\text{Zn}_{3-x}\text{Al}_x)^{\text{oct}}(\text{Si}_{2-x}\text{Al}_x)^{\text{tet}}\text{O}_5(\text{OH})_4$ [12].

In summary, this work gives an example of 'soft chemistry routes [13]' of sepiolite clay mineral to catalytic materials from the standpoint of inorganic chemistry. In future, this method is applicable and extended to other similar minerals, such as palygorskite, and other cations, such as Mn^{2+} , Cu^{2+} , fixed by 'a size-memory effect' to make a novel functional materials as well as catalysts.

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