

Separation and Recovery of Tetramethyl Ammonium Hydroxide with Zeolitic Adsorbents

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Received: 4.2.2010; Accepted 17.3.2010; Published 24.3.2010

ABSTRACT

Separation and recovery of tetramethyl ammonium hydroxide (TMAH) has been investigated, employing several zeolites as adsorbents. Zeolite X, prepared by using TMAH as a structure directing agent, possesses highest adsorption ability among the adsorbents investigated in the present work, which corresponds to the specific surface area and pore volume of the zeolite. The adsorption amount of TMAH with the zeolitic adsorbents increases with increase in pH value in the aqueous solution, indicating the adsorption progresses *via* cation exchange mechanism. The chromatographic operation is finally conducted, using granulated zeolitic adsorbents to prevent from the pressure-drop, and the quantitative adsorption-elution processing of TMAH can be achieved.

Keywords: Adsorption; tetramethyl ammonium hydroxide; zeolite

INTRODUCTION

Tetramethyl ammonium hydroxide (TMAH) has been widely used as a developer on the manufacture of semiconductor devices and liquid crystal displays. The treatment of the waste solution containing TMAH recently becomes important issue from the environmental protection point of view, since the TMAH is toxic organic alkali. There are several reports and patents concerning the treatment process of the waste TMAH solution, based on reverse osmosis¹ and electrodialysis.^{2,3} The alternative treatment process, especially at the end-of-pipe of the manufacture industry, is still required, since the current treatment processes are quite complicated. The ion exchange method has therefore been started to be investigated for the recovery and recycle of TMAH. Shibata *et al.* have investigated the recovery of TMAH with commercial ion exchange resins. The cation exchange resin was applied for the selective recovery of TMAH. The anion exchange resin was then employed for the regeneration of TMAH, since TMA⁺ existed as chloride in the eluent solution from the cation exchange resin.⁴ Similar process, employing ion exchange resin, has been also patented.⁵ Kelleher *et al.* have

prepared cubic mesoporous silicate for investigating the fundamental adsorption property of TMAH.⁶

In the present work, the zeolitic adsorbents, for the selective recovery of TMAH, have been prepared. The zeolitic adsorbents were prepared by hydrothermal synthesis and were characterized by XRD, FE-SEM, and N₂ adsorption. The adsorption behavior of TMAH was then investigated by batchwise method. The granulated zeolitic adsorbents were finally applied for the column operation for investigating the selective recovery process of TMAH from waste water.

EXPERIMENTAL

Synthesis of Zeolitic Adsorbents

Tetramethyl ammonium hydroxide (TMAH) was supplied by Tokyo Chemical Industry. All other chemicals used were supplied by Wako Pure Chemical Industries, as analytical-grade reagents. The chemicals were used without further purification. Zeolitic adsorbents, zeolite A (Na-A) and zeolite X (Na-X), were prepared by hydrothermal synthesis. Sodium aluminate (10.0 g for Na-A and 5.45 g for Na-X) and sodium silicate (14.0 g for Na-A and 15.0 g for

Na-X) were respectively dissolved in 100 mL of 2 mol/L sodium hydroxide solution. The two solutions were mixed in a Teflon vessel of stainless-steel autoclave, and then hydrothermally synthesized at 373 K for 24 h. The autoclave was immediately cooled down, and then the products were filtrated, washed, and dried at 333 K for overnight.

The counter cation of the zeolites was exchanged with divalent cations, such as calcium and strontium ions.⁷ Zeolites (Na-A and Na-X) of 0.5 g and 30 mL of 0.25 mol/L strontium chloride or calcium chloride solution were shaken for 3 h at 298 K. The zeolites were then washed and dried at 333 K, to obtain the counter cation exchanged zeolite A (Sr-A and Ca-A) and zeolite X (Sr-X and Ca-X). TMAH-templated zeolite A and X were also prepared (Templated-A and Templated-X). Each 10 mL of sodium aluminate solution and sodium silicate solution and 10 mL of 1 mol/L TMAH solution were mixed in the autoclave and hydrothermally synthesized at 373 K for 24 h. The dried product was calcined at 823 K for 72 h, to remove the TMAH template. The zeolites obtained were characterized by field emission scanning electron microscope (Hitachi S-5200), X-ray diffraction (Rigaku RINT-2000), and volumetric nitrogen gas adsorption (Bell Japan BELSORP-mini).

In the case of chromatographic operation, the granulated adsorbent is preferred, due to suppression of pressure drop through the packed column. The 6.5 g of powder type of Templated-X was mixed with 3.5 g of alumina based binder (CATALOID AP-1, Catalysts & Chemicals Industries) together with small amount of deionized water. The kneaded mixture was pressed out from 1 mm hole in diameter by the extruder, and dried at room temperature for overnight. The mixture was then calcined at 823 K for 3 h, and then was cut for 0.5 – 1 mm in length.

Adsorption of TMAH

The batchwise adsorption of TMAH was carried out by contacting 0.05 g of each powder type zeolite and 10 mL of TMAH aqueous solution. The mixture was shaken at 298 K for 24 h. The adsorption ability with alumina based binder, after calcinations at 823 K for 3 h, is also examined by the same manner. The concentration of TMAH was analyzed by an ion chromatograph (Metrohm Compact IC 761type), and the corresponding adsorption amounts, q , were determined by material balance, as follows.

$$q = \frac{([\text{TMAH}]_{\text{initial}} - [\text{TMAH}]) \cdot L}{w}$$

where $[\text{TMAH}]_{\text{initial}}$ and $[\text{TMAH}]$ are initial and equilibrium concentrations of TMAH in the aqueous phase, L is volume of aqueous solution, and w is weight of adsorbent. The pH of aqueous phase was measured with a pH meter (Horiba F-23).

The chromatographic operation was also conducted using granulated Templated-X. The granulated adsorbent (ca. 0.4 g) was packed into the column tube (5 cm in length and 5 mm in inner diameter) together with quartz wool to be sandwiched. The feed aqueous solution, containing 10 mg/L of TMAH or 10 mg/L of both TMAH and phenol at pH = 10, was fed upward to the column using a dual-plunger pump at 0.1 mL/min (Flom KP-11). The effluent was collected with a fraction collector (Advantec CHF122SA), to measure the concentrations of TMAH by ion chromatograph and of phenol with UV-Vis spectrophotometer at wavelength 210 nm (JASCO V-660). After the breaking through, the TMAH loaded in the adsorption column was eluted with 0.01 mol/L of HCl. Bed volume of the effluent is calculated by:

$$\text{Bed Volume} = \frac{v \cdot t}{V}$$

where v is flow rate of solution, t is supplying time of feed solution, and V is the wet volume of adsorbent.

RESULTS AND DISCUSSION

Preparation and Characterization of Zeolitic Adsorbents

Figure 1 shows the SEM photographs of zeolites obtained. In the case of Na-A, cubic shape particles with 0.5 – 1.0 μm are obtained,

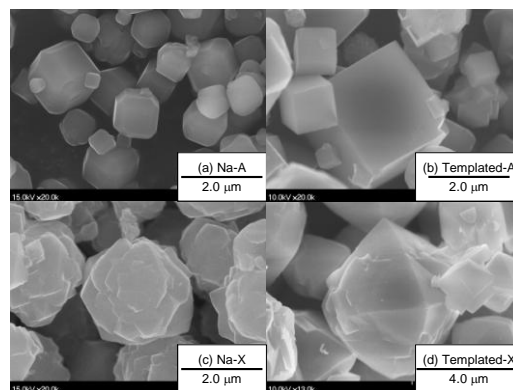


Figure 1. SEM photographs of zeolitic adsorbents for (a) Na-A, (b) Templated-A, (c) Na-X, and (d) Templated-X.

Table 1. Characteristics and maximum adsorption amount of zeolitic adsorbents.

	Specific surface area* (m ² /g)	Pore volume* (cm ³ /g)	q_{\max}^{\dagger} (mmol/g)
Na-A	-	-	7.59×10^{-3}
Sr-A	568	0.28	-
Ca-A	642	0.32	-
Templated-A	-	-	9.88×10^{-3}
Na-X	640	0.33	7.79×10^{-3}
Sr-X	649	0.32	-
Ca-X	722	0.36	-
Templated-X	727	0.35	1.13×10^{-2}

* The data were obtained from BET analysis.

[†] The equilibrium pH values are 10.38 ± 0.15 (Na-A), 10.45 ± 0.13 (Templated-A), 10.43 ± 0.17 (Na-X), 10.39 ± 0.17 (Templated-X).

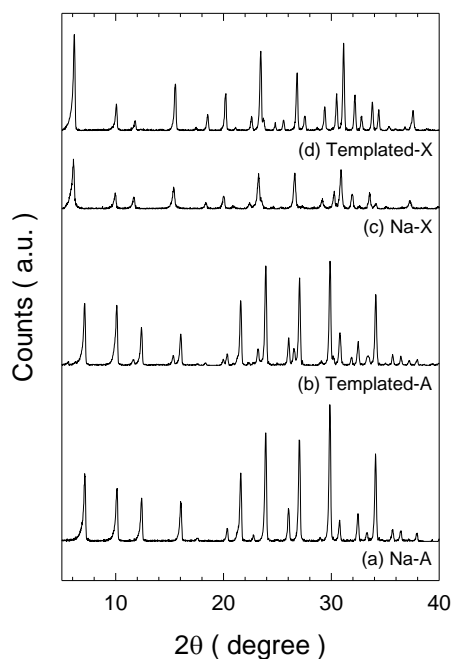


Figure 2. XRD patterns for zeolitic adsorbents for (a) Na-A, (b) Templated-A, (c) Na-X, and (d) Templated-X.

while aggregated octahedron particles with ca. 2 μm are obtained in the case of Na-X. The particle size of Templated-A and Templated-X becomes larger, though the morphologies of both template zeolites are almost the same. Figure 2 shows the XRD patterns of the zeolitic adsorbents. Comparing the XRD patterns with the database,⁸ the zeolitic structures could be obtained by the present hydrothermal synthesis. Figure 3 shows the N₂ adsorption isotherms of the zeolitic adsorbents. In the case of zeolite As, almost no N₂ adsorption progresses on Na-A and a little N₂ adsorption progresses on Templated-A, while the sufficient N₂ adsorption was observed for Sr-A and Ca-A. This is because the diameter

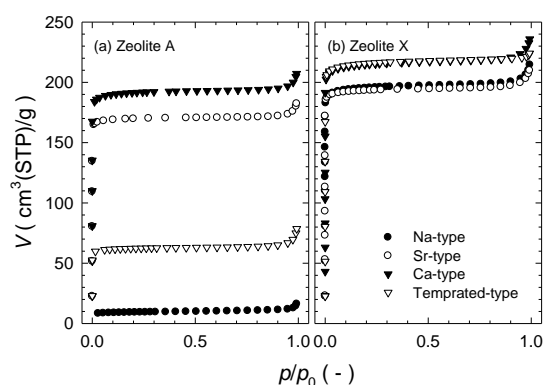


Figure 3. N₂ adsorption isotherms on zeolitic adsorbents for (a) zeolite A and (b) zeolite X.

of mouse of the pore increases when the counter cation of zeolite A was exchanged from Na⁺ to divalent cations.⁷ Alternatively, sufficient N₂ adsorption progresses in all cases of zeolite Xs. The specific surface area and pore volume, determined by BET analysis, are listed in Table 1. Ca-X and Templated-X have high surface area and pore volume among the zeolites prepared in this work.

Batch Adsorption of TMAH

In preliminary experiments, we confirmed that the adsorption attained equilibrium within 24 h. Figure 4 shows the effect of pH on the adsorption amount of TMAH. The adsorption amount of TMAH increases with increase in pH in all zeolites. This indicates that the adsorption of TMAH on the zeolitic adsorbent progresses *via* cation exchange reaction. In addition, zeolites are suitable as the adsorbent for TMAH, since the pH value of the practical waste solution containing TMAH is alkaline region. The adsorption abilities of TMAH on the zeolitic adsorbents mostly correspond to the order of

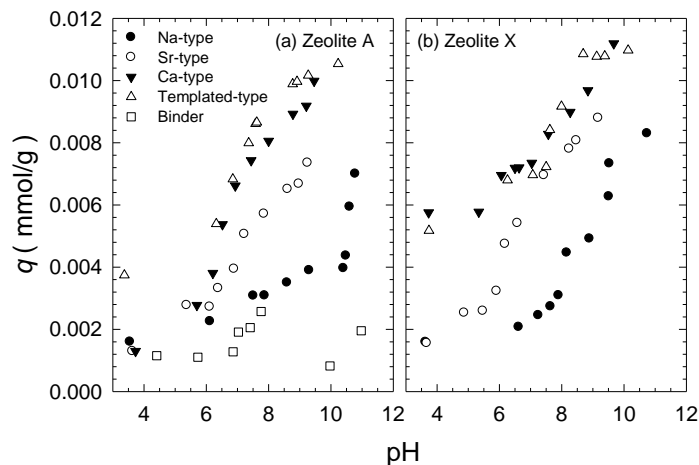


Figure 4. Effect of equilibrium pH on the adsorption amount of TMAH on (a) zeolite A and alumina based binder and (b) zeolite X; $[TMAH]_{initial} = 10 \text{ mg/L}$.

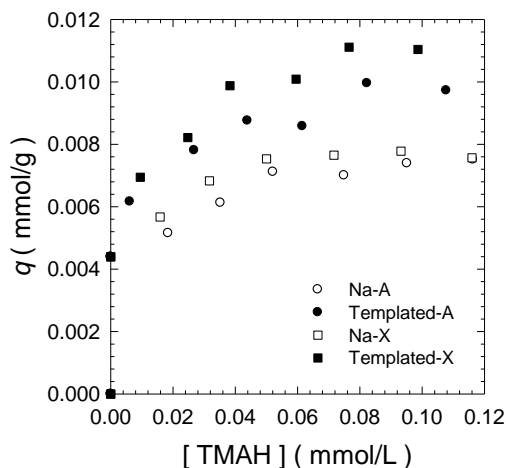


Figure 5. Adsorption isotherms of TMAH with Na-A, Templated-A, Na-X, and Templated-X. The equilibrium pH values are 10.38 ± 0.15 (Na-A), 10.45 ± 0.13 (Templated-A), 10.43 ± 0.17 (Na-X), 10.39 ± 0.17 (Templated-X).

specific surface area and pore volume shown in Table 1. The specific surface area and pore volume are therefore concluded as the important factors affecting the adsorption amount of TMAH.

The adsorption isotherms at $\text{pH} = \text{ca. } 10$ were obtained for Na-A, Templated-A, Na-X, and Templated-X, as shown in Figure 5. The adsorption is revealed to progress with Langmuir adsorption mechanism in all cases, and the maximum adsorption amounts, q_{max} , were listed in Table 1. Based on the batchwise adsorption, Templated-X possesses the highest adsorption capacity for TMAH. The lower adsorption capacity of the present zeolitic adsorbents, compared with the commercial ion exchange

resin,⁴ may be because the pore diameter of the present zeolitic adsorbents is small (sub nm order). The adsorption capacity is expected to be improved, when the inorganic adsorbents having larger pore diameter as well as larger specific surface area and pore volume, are developed.

Chromatographic Separation of TMAH

Chromatographic separation of TMAH is conducted with Templated-X granulated with alumina based binder. The preliminary experiments for the adsorption of TMAH with the binder are carried out, followed by the calcinations of the binder at 823 K for 3 h, which are shown in Figure 4(a). Almost no adsorption progresses on binder alone.

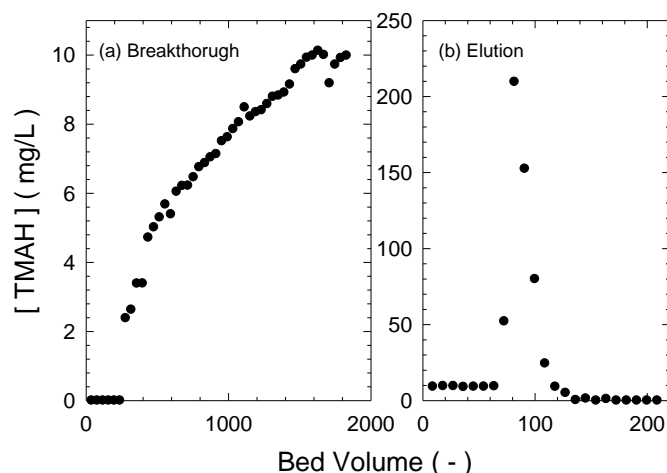


Figure 6. (a) Breakthrough and (b) elution profiles of TMAH in single system; $[TMAH]_{initial} = 10 \text{ mg/L}$.

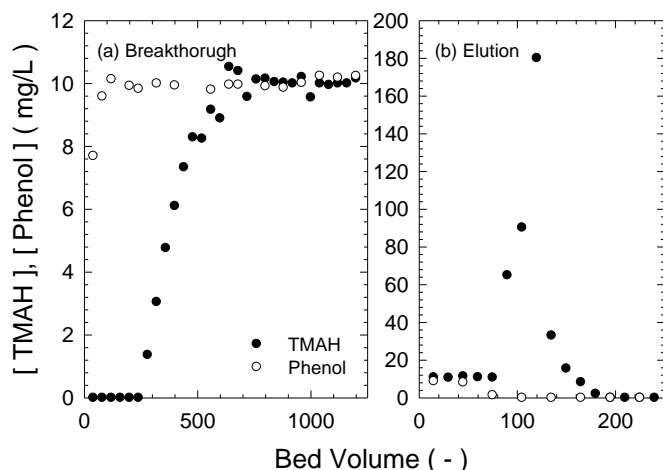


Figure 7. (a) Breakthrough and (b) elution profiles of TMAH and phenol in binary system; $[TMAH]_{initial} = [Phenol]_{initial} = 10 \text{ mg/L}$.

The breakthrough and elution curves are shown in Figure 6. TMAH is completely adsorbed on Templated-X until Bed Volume = ca. 230, and then the concentration of TMAH in the effluent increases gradually. The elution of TMAH was then conducted with 0.01 mol/L HCl. The TMAH adsorbed on the Templated-X is quantitatively eluted by HCl. The maximum concentration at the elution stage was reached up to 210 mg/L, indicating 21 times concentration of TMAH can be achieved.

The effect of co-existed component, phenol, on the chromatographic separation of TMAH is also investigated, since the actual waste solution of TMAH includes phenol.⁴ Figure 7 shows the breakthrough and elution

curves of TMAH and phenol with the Templated-X. Phenol is scarcely adsorbed on the zeolitic adsorbent, because phenol is existed as anionic species in alkaline region. The selective recovery of TMAH can be achieved by single adsorption-elution processing, and the TMAH is quantitatively recovered in single elution stage.

CONCLUSIONS

The zeolitic adsorbents were prepared and were employed as the adsorbents for TMAH, with following results. The adsorption of TMAH with the zeolitic adsorbents progresses *via* cation exchange mechanism. Since the adsorption amount of TMAH mostly corresponds to the specific surface area and pore volume of the

adsorbents, Templated-X possesses the highest adsorption amount among the adsorbents investigated. The chromatographic operation was conducted using the granulated Templated-X, and the selective adsorption-elution of TMAH against phenol can be achieved by single adsorption-elution processing. The inorganic adsorbents based on the ion exchange mechanism shows the potential for the selective recovery of TMAH, even though the adsorption amount is low. The adsorption amount would be improved, when the inorganic adsorbents having larger specific surface area, pore volume, and pore diameter are developed.

ACKNOWLEDGEMENT

The authors are grateful for the financial support by Grant-in-Aid for Young Scientists (B) (No. 19760530) from Japan Society for the Promotion of Science (JSPS). The authors are grateful to Professor Katsutoshi Yamamoto of The University of Kitakyushu for his discussion on the characterization of zeolites and to Professor Sachio Asaoka of The University of Kitakyushu for his suggestion in the granulation of zeolitic adsorbents. The XRD measurement, SEM analysis, and N₂ adsorption were

performed at the Instrumentation Center, The University of Kitakyushu.

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