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SYTHESIS AND SORPTION PROPERTIES OF ZEOLITE ZSM-5

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By

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Zeolite ZSM-5 was synthesised by using SDS or the mixture of TPA/SDS as
a templating agent. There is no significant difference in the X-Ray Diffraction
(XRD) pattern observed among zeolites synthesised using different templating
agents. This indicated that zeolites of similar crystallinity were formed. However,
slightly different surface area, porosity and morphology of the zeolites were
observed, when different ratio of TPA/SDS were used as a templating agents.
Zeolites A, X and ZSM-5 were found to be an effective ion exchanger for lanthanum
and yttrium ions from aqueous solutions. High metal ion uptake was achieved at
initial pH solution of 4.0-4.5 with different conditions to avoid chemical
precipitation. The microwave-assisted method showed that it could accelerate the
metal sorption process by about 500 times compared to the conventional method.
The zeolites loaded with lanthanum and yttrium ions significantly improved the
sorption capacity of zeolite towards arsenic ions. Experimental conditions such as

pH, initial concentrations, adsorbent dosage and temperature have been optimised to utilise zeolite as an adsorbent for the removal of arsenate ion from aqueous solution. All data fitted the Langmuir and Freundlich isotherms. The zeolites were found to be an ineffective color removal agent for natural peat water and humic acid.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Master Sains.

SINTESIS DAN CIRI-CIRI ERAPAN ZEOLIT ZSM-5

Oleh

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Zeolit ZSM-5 telah disintesis dengan menggunakan SDS ataupun campuran
TPA/SDS sebagai agen acuan. Tiada perbezaan yang ketara dalam corak belauan
sinar x-raynya (XRD) diantara zeolit-zeolit yang disentesis menggunakan agen-agen
acuan berbeza. Ini membuktikan bahawa zeolit ZSM-5 dengan kristal yang serupa
telah terbentuk. Perbezaan dari segi keluasan, keliangan dan morfologi telah
diperhatikan apabila nisbah yang berbeza bagi TPA/SDS digunakan. Zeolit-zeolit A,
X dan ZSM-5 didapati amat sesuai digunakan sebagai penukar ion bagi ion-ion
lantanum dan itrium dalam larutan akuas. Penukaran ion yang tinggi dapat diperolehi
pada pH awal 4.0-4.5 dengan pembolehubah-pembolehubah yang berlainan untuk
menghalang pemendakan secara kimia. Kaedah berbantukan mikrogelombang boleh
digunakan untuk memacu proses erapan sehingga 500 kali lebih pantas berbanding
dengan kaedah konvensyenal. Zeolit-zeolit yang dipadukan dengan ion logam
lantanum dan itrium didapati dapat meningkatkan kapasiti erapan terhadap ion

arsenik. Beberapa pembolehubah ekperimen seperti pH, kepekatan bahan pemula, perubahan berat penjerap dan suhu telah digunakan untuk mengkaji zeolit sebagai penyingkir ion arsenat dalam larutan akuas. Semua data-data telah dipadankan dengan isoterma-isoterma Langmuir dan Freundlich. Zeolit-zeolit didapati tidak sesuai sebagai agen penyingkir warna untuk air tanah semulajadi dan asid humik.

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LIST OF ABBREVIATIONS

α	:	Limiting amount of metal ion that can be taken per mass of adsorbent
ΔE_{ab}	:	Color difference unit
ΔE_{ab}- A	:	Color difference value for zeolite A
ΔE_{ab}-X	:	Color difference value for zeolite X
A-La	:	Sorption of Lanthanum on zeolite A
ALa-As	:	Sorption of Arsenate ion on Lanthanum-loaded zeolite A
A-Y	:	Sorption of Yttrium on zeolite A
AY-As	:	Sorption of Arsenate ion on Yttrium-loaded zeolite A
BET	:	Brunnauer Emmet Teller
C_e	:	Metal ion concentration at equilibrium (mM)
C_i	:	Initial metal ion concentration (mM)
EC	:	Euhedral Crystal
HA	:	Humic acid
K_F	:	Constant of Freundlich equation
K_L	:	Constant of Langmuir equation
n	:	Parameter of Freundlich equation
n_m	:	Monolayer capacity
P	:	Pressure
P^o	:	Saturation pressure
PW	:	Peat water
pH_e	:	pH value at equilibrium
q_e	:	Capacity (mmol/g)

r	:	Correlation coefficient
S	:	Amount of zeolite (g)
SA	:	Spherulitic Agglomerates
t	:	Time
V	:	Volume of the solution (L).
X-La	:	Sorption of Lanthanum on zeolite X
XLa-As	:	Sorption of Arsenate ion on Lanthanum-loaded zeolite X
X-Y	:	Sorption of Yttrium on zeolite X
XY-As	:	Sorption of Arsenate ion on Lanthanum-loaded zeolite X
ZSM-5(S)La-As	:	Sorption of Arsenate ion on Lanthanum-loaded zeolite ZSM-5 with SDS as a templating agent
ZSM-5(S)Y-As	:	Sorption of Arsenate ion on Yttrium-loaded zeolite ZSM-5 with SDS as a templating agent
ZSM-5(T)La-As	:	Sorption of Arsenate ion on Lanthanum-loaded zeolite ZSM-5 with TPA as a templating agent
ZSM-5(T)Y-As	:	Sorption of Arsenate ion on Yttrium-loaded zeolite ZSM-5 with TPA as a templating agent
ZSM-5(S)-La	:	Sorption of Lanthanum on zeolite ZSM-5 with SDS as a templating agent
ZSM-5(S)-Y	:	Sorption of Yttrium on zeolite ZSM-5 with SDS as a templating agent
ZSM-5(T)-La	:	Sorption of Lanthanum on zeolite ZSM-5 with TPA as a templating agent
ZSM-5(T)-Y	:	Sorption of Yttrium on zeolite ZSM-5 with TPA as a templating agent

CHAPTER 1

INTRODUCTION

1.1 Zeolites

Zeolites are crystalline, hydrated aluminosilicate minerals containing exchangeable alkaline and alkaline earth metal cations normally of group I and group II elements, in particular, sodium, potassium, magnesium, calcium, strontium, and barium, as well as water molecules in their structural frameworks. Structurally, they are complex, porous, crystalline inorganic polymers, enclosing interconnected cavities in which the metal ions and water molecules are contained. They are based on an infinitely extending three dimensional network of AlO_4 and SiO_4 tetrahedra linked to each other by sharing all the oxygen ions [1].

Zeolites may be represented by an empirical formula of $M_{2/n}Al_2O_3xSiO_2.yH_2O$. In this oxide formula, x is generally equal to 2 or greater since AlO_4 tetrahedra are joined only to SiO_4 tetrahedra, n is the cation valence which neutralize the negative charge on the aluminosilicate framework and y represents the water contained in the voids of the zeolite [2].

The framework contains channels and interconnected voids that are occupied by the cation and water molecules. The cations are quite mobile and may usually be exchanged, to varying degrees, by other cations. Intracrystalline 'zeolitic' water in many zeolites is removed continuously and reversibly, generally by the application of heat, which leaves intact a crystalline host structure permeated by

micropores which may amount to 50% of the crystals by volume. In many other zeolites, mineral and synthetic, cation exchange or dehydration may produce structural changes in the framework.

A Swedish mineralogist Baron Axel Cronstedt first described zeolite as a mineral group in 1756. He named the mineral zeolite from the greek words *zeo* and *lithos* which means to boil and stone, respectively. Cronstedt observed that on heating with a blowtorch the zeolites hissed and bubbled as though they were boiling [2].

Zeolites are important inorganic materials, which have excellent catalytic as well as separation properties. Several properties of zeolite minerals have been studied, including adsorption and ion exchange. These were important applications of zeolites for removal of heavy metals by both processes. Among others, the advantages of ion exchange over the chemical precipitation method are high selectivity, can be recovered and produce less sludge. The availability of natural zeolites provides a low cost ion exchanger [3].

1.1.1 Type of Zeolite

Naturally, zeolite minerals are formed over much of the earth's surface, including the sea bottom. They were considered as typically occurring in nature in vugs and vesicles of basaltic lava in specific kinds of rocks subjected to moderate geologic temperature and pressure (the metamorphic zeolite facies) and in altered and reacted volcanic ash deposits [4]. They were widely used until 1948 when the

first pure synthetic of mordenite was synthesised, while zeolites A, X and Y were synthesised by Union Carbide in 1956-64 and highly siliceous zeolite ZSM-5 (Zeolite Scony Mobil) was synthesised by Mobil Oil Corporation in 1972 [5]. Table 1 showed a few examples of zeolite composition [6].

Table 1: Zeolite Compositions

Zeolite	Typical formula
Natural	
Mordenite	$Na_8[AlO_2)_8(SiO_2)_{40}].24H_2O$
Faujasite	$(Ca,Mg,Na_2,K_2)_{4.5}[AlO_2)_{59}(SiO_2)27].27H_2O$
Clinoptilolite	$Na_6[(AlO_2)_6(SiO_2)_{30}].24H_2O$
Synthetic	
Zeolite A	$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}].27H_2O$
Zeolite X	$Na_{86}[(AlO_2)_{86}(SiO_2)_{106}].264H_2O$
Zeolite ZSM-5	$(Na,TPA)_3[(AlO_2)_3(SiO_2)_{93}].16H_2O$

1.1.2 Structure of Syntbetic Zeolite

The fundamental building block of all zeolites is a tetrahedron of four oxygen anions surrounding a small silicon or aluminium ion. These tetrahedra are arranged so that each of the four oxygen anions is shared in turn with another silica or alumina tetrahedron to form a wide range of small secondary building units. The crystal lattice extends in three dimensions and the -2 oxidation state of each oxygen is accounted for. Each silicon ion has its +4 charge balanced by the four tetrahedral oxygen's and the silica tetrahedra and therefore electrically neutral.

Each alumina tetrahedron has a residual charge of -1 since the trivalent aluminium is bonded to four oxygen anions. It requires a + 1 charge from a cation in the structure to maintain neutrality. Figure 1(a) shows the primary building units of

zeolite. In these structural diagrams the corners of the polyhedra represent Si or Al atoms, and the connecting lines represent the shared oxygen atoms. The cations are usually sodium in zeolites as it is initially prepared, but they are readily replaced via ion exchange. This cation is not locked into the framework by a 'box' of four oxygen atoms as in the Si^{4+} or Al^{3+}. These charge compensating cations are relatively mobile and can in many cases easily exchanged for other cations [6]. Ion exchange represents the most direct and useful method for the alteration of zeolite properties.

Many zeolite structures are based on a secondary building unit that consists of 24 silica or alumina tetrahedra linked together. For example 4 and 6 rings linked together to form a basket like structure called a truncated octahedron. This is a sodalite unit (or β-cage) as shown in figure 1(b). Several of the most important zeolite structures are based on the sodalite unit (a truncated octahedron). Different combinations of the same secondary building unit may give numerous distinctive zeolites.

The structure of a synthetic zeolite, zeolite A is shown in figure 1(c). Oxygen bridges between the 4 rings linked each sodalite unit. A three dimensional network of linked cavities forming channels is formed. The free pore aperture of zeolite A is determined by an eight member oxygen ring and it has a free pore diameter of 4.2 Å [7].

The structure of faujasite [7], a naturally occurring mineral, is shown in figure 1(d). The sodalite units are linked by oxygen bridges between four of the

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eight 6 rings in a tetrahedral array, forming hexagonal prisms. The truncated octahedra are stacked similar to those carbon atoms in diamond. This structure result in a supercage (sorption cavity) surrounded by ten sodalite units, which is sufficiently large for an inscribed sphere with a diameter of 12 Å.

The framework of ZSM-5 which were determined by Kokotailio *et al.* [8] contains a novel configuration of linked tetrahedra shown in figure 1(e) and consisting of eight five membered rings. Then, the ZSM-5 units join through edges to form chains. The chains can be connected to form sheets and the linking of the sheet lead to a three dimensional framework structure. The chains extend along the z-axis. The generic name 'pentasil' has been given to designate these solids, irrespective of minor differences in crystal structure. The ZSM-5 framework contains two intersecting channel systems, one sinusoidal running parallel to 001 and the other straight and parallel to 010.

1.1.3 Si/Al Ratios

The Si/Al ratio of a zeolite could showed the changes of its cation content; the fewer aluminium atoms there are, the fewer the exchangeable cations will be present. The highly siliceous zeolites such as zeolite ZSM-5 can have a Si/Al ratio that lies between 20 and ∞. Zeolite A and X have Si/Al ratio of 1. Zeolites with high Si/Al ratios are stable in the presence of concentrated acids but not to those with lower Si/Al ratios (in ratio 1-1.5) [7].