Investigation on the Effect of the Cation Counterion used on the Ion Exchange Efficiency with HZSM-5

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Abstract

In this study the efficiency of the ion exchange process of HZSM-5 with copper and zinc cations was investigated. It was found that...

1   Aim

This project aims to investigate how the efficiency of the ion exchange process is effected by the cation being exchanged. Specifically the copper and zinc cation exchange processes of an HZSM-5 zeolite were compared.

2   Introduction

Zeolites are crystalline, microporous solids used for a large number of purposes such as for catalytic cracking, air purification, water softening and desiccants.[1,2] This project was completed using the ZSM-5 (Zeolite Socony Mobil-5)[3] zeolite which has important uses in the petrochemical industry such as for the conversion of methanol to gasoline, dewaxing of distillates, separation of organic products (such as separating para-xylene from its isomers), the interconversion of hydrocarbons.[4–6]

2.1   Structure

Each zeolite is comprised of a finite or infinite number of unique unit cells each of which is made from a constant, integral number of the same type of secondary building unit (SBU) with each vertex in the SBU being a tetrahedron of either $[SiO_4]$ or $[AlO_4]^-$ (which are themselves the primary building units).[2,7–10] Each aluminium tetrahedron in a SBU introduces a negative charge – since aluminium has a 3+ oxidation state compared the 4+ oxidation state of silicon – which is balanced by the presence of cationic counterions.[2,9–11] The ZSM-5 zeolite used is a pentasil[4,10] zeolite (constructed of eight five-membered rings)

with an SBU containing twelve AO_4 tetrahedra which form a pair of five-one units[4,7,12] as shown in figure 1 (A-O-A bridges are shown as straight lines to increase the clarity of the images and since the A-O-A bond angle is around $140\text{–}150° \approx 180°$ for silicas and aluminosilicates and the A atoms are represented by the vertices).[7]
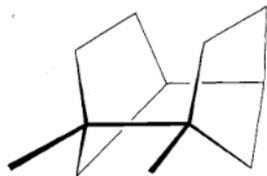

Figure 1: Secondary building unit for ZSM-5 zeolite.[4]

These SBUs then form long chains (figure 2) which then themselves interconnect to form layers hence giving a unit cell containing eight SBUs figure 3.[4] In 3 one of the chains (shown in figure 2) is highlighted to demonstrate how the chains interconnect to form layers.
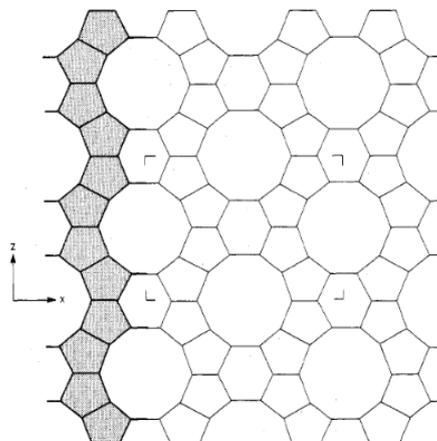

Figure 2: Chain building unit for ZSM-5 zeolite.[4]

Figure 3: Layer of ZSM-5 zeolite.[4]

Since there are eight SBUs of twelve tetrahedra per unit cell there are $8 \times 12 = 96$ A atoms and there are two oxygen atoms per individual A atom in the cell[13] so per unit cell there are $2 \times 96 = 192$ oxygen atoms.[7] This gives the unit cell formula given in 2.1.1

where X is a cation with a charge of q, hence $\frac{1}{q}$ of these cations are required per negative charge.[14]

$$X_{\frac{n}{q}} Al_n Si_{96-n} O_{192} \cdot x\, H_2O \tag{2.1.1}$$

2.2 Ion-Exchange

These X^{q+} cations can be exchanged with other ions in a process called ion-exchange. Changing the counterion of the ZSM-5 zeolite can alter the acidity, hydrophobicity, reaction selectivity and other properties of the zeolite.[5,9,15]

The copper exchanged form of ZSM-5 is known to be one of the best forms of ZSM-5 for the selective catalytic reduction of NO by C_2-C_4 hydrocarbons.[14,16,17] This is an important use case since large amounts of NO are produced in vehicle and industrial boiler emissions and NO is known to cause air pollution and acid rain.[18]

Similarly the zinc exchanged form of ZSM-5 is currently subject to much research since it has been found to be effective at selectively converting methanol to use aromatic species such as benzene, toluene and xylene (important for the manufacture of polyester fibers, dyes, pesticides and medicines) as an alternative method to petroleum processing.[19,20] Specifically ZnZSM-5 has – so far – been the best choice of cation for this purpose since it is cheap, non-toxic and highly effective at the aforementioned aromatization process.[21]

A ZSM-5 zeolite with a SiO_2/AlO_3 ratio of 23 was used since this maximised the number of sites which were available for ion-exchange due to the higher aluminium content. In addition this increased the efficiency of the ion-exchange process since zeolites with a high Si/Al ratio are hydrophobic[9,22,23] hence the cation solution does not spontaneously enter the zeolite nanopores so ion-exchange happens only at sites close to the pore entrance.[9,23] This will thus reduce the percentage uncertainties in the values recorded.

3 Experimental

Standard solutions of Cu^{2+} and Zn^{2+} ($50.00\,cm^3$) were made using $CuSO_4 \cdot 5\,H_2O$ and $ZnSO_4 \cdot 7\,H_2O$ with concentration $2.008 \times 10^{-3}\,mol\,dm^{-3}$ and $2.02 \times 10^{-3}\,mol\,dm^{-3}$ respectively. The absorbance of the standard copper sulphate solution was taken at $806\,nm$ (0.484) then $20.00\,cm^3$ of the standard solutions were added to $0.4810\,g$ (for the copper solution) and $0.5274\,g$ (for the zinc solution) of HZSM-5 zeolite with an $AlO_3:SiO_2$ ratio of 23 – forming an opaque white suspension – before heating both solutions (with stirring) at $70\,°C$ for one hour. Centrifugation was completed on part of the resultant copper mixture, however time constraints prevented the completion of this process. The

two mixtures were thus stored in a fridge for one week until the following laboratory session.

After one week the zeolite had settled in the bottom of the solutions. The clear solution was decanted and the remainder was centrifuged for 30 minutes before the supernatant was reintroduced to the initially decanted solution producing a slightly cloudy copper solution and a moderately cloudy zinc solution. The solutions were made up to $100.00\,\mathrm{cm^3}$ before the absorbance of the copper solution at $806\,\mathrm{nm}$ was determined (0.110) and the zinc solution was titrated against a standard EDTA solution ($0.4993\,\mathrm{mol\,dm^{-3}}$) with $2\,\mathrm{cm^3}$ of a pH 10 buffer solution and eriochrome black T as the indicator.

4 Results

4.1 Copper-Exchanged Zeolite

Table 1: Masses used.

Substance	Mass / g
$CuSO_4 \cdot 5\,H_2O$	0.5014
HZSM-5	0.4810

Table 2: Spectrophotometric results.

Substance	Absorbance
Standard Solution	0.484
Post-Reaction Solution	0.110

Let $V_{\mathrm{Cu_{std.}}}$ be the volume and $[CuSO_4]_{\mathrm{std.}}$ be the concentration of the standard Cu^{2+} solution.

$$n_{\mathrm{CuSO_4}} = \frac{m_{\mathrm{CuSO_4 \cdot 5\,H_2O}}}{Mr_{\mathrm{CuSO_4 \cdot 5\,H_2O}}}$$

$$[CuSO_4]_{\mathrm{std.}} = \frac{n_{\mathrm{CuSO_4}}}{V_{\mathrm{Cu_{std.}}}}$$

$$= \frac{m_{\mathrm{CuSO_4 \cdot 5\,H_2O}}}{V_{\mathrm{Cu_{std.}}} Mr_{\mathrm{CuSO_4 \cdot 5\,H_2O}}} \tag{4.1.1}$$

Rearranging the Beer-Lambert law (equation 4.1.2) for the molar extinction coefficient:

$$A = \epsilon c l \tag{4.1.2}$$

$$\epsilon = \frac{A}{cl} \tag{4.1.3}$$

Hence using equations 4.1.1 and 4.1.3 with $A_{\text{Cu}_{\text{std.}}}$ being the absorbance of the standard $CuSO_4$ solution:

$$
\begin{aligned}
\epsilon_{CuSO_4} &= \frac{A_{\text{Cu}_{\text{std.}}}}{[CuSO_4]_{\text{std.}}l} \\
&= \frac{A_{\text{Cu}_{\text{std.}}}V_{\text{Cu}_{\text{std.}}}Mr_{CuSO_4 \cdot 5\,H_2O}}{lm_{CuSO_4 \cdot 5\,H_2O}}
\end{aligned}
\tag{4.1.4}
$$

This hence gives:

$$
\begin{aligned}
\epsilon_{CuSO_4} &= \frac{0.484 \times 50.00 \times 10^{-3}\,\text{dm}^3 \times (63.546 + 32.066 + 4(15.999) + 5(2(1.008) + 15.999))\,\text{g mol}^{-1}}{1.0\,\text{cm} \times 0.5014\,\text{g}} \\
&= \frac{0.484 \times 50.00 \times 10^{-3}\,\text{dm}^3 \times 249.677\,\text{g mol}^{-1}}{1.0\,\text{cm} \times 0.5014\,\text{g}} = 12.05\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}
\end{aligned}
\tag{4.1.5}
$$

By rearranging the Beer-Lambert Law (equation 4.1.2) for concentration:

$$
c = \frac{A}{\epsilon l}
\tag{4.1.6}
$$

Letting $[CuSO_4]_{\text{prod.}}$ be the concentration, $A_{\text{Cu}_{\text{prod.}}}$ be the absorbance, $n_{\text{Cu}_{\text{prod.}}}$ be the amount of Cu^{2+} ions and $V_{\text{Cu}_{\text{prod.}}}$ be the volume of the solution after the ion-exchange reaction while using equation 4.1.6:

$$
\begin{aligned}
[CuSO_4]_{\text{prod.}} &= \frac{A_{\text{Cu}_{\text{prod.}}}}{\epsilon_{CuSO_4}l} \\
n_{\text{Cu}_{\text{prod.}}} &= [CuSO_4]_{\text{prod.}}V_{\text{Cu}_{\text{prod.}}} \\
&= \frac{A_{\text{Cu}_{\text{prod.}}}V_{\text{Cu}_{\text{prod.}}}}{\epsilon_{CuSO_4}l}
\end{aligned}
\tag{4.1.7}
$$

Substituting equation 4.1.4 into 4.1.7:

$$
n_{\text{Cu}_{\text{prod.}}} = \frac{A_{\text{Cu}_{\text{prod.}}}V_{\text{Cu}_{\text{prod.}}}m_{CuSO_4 \cdot 5\,H_2O}}{A_{\text{Cu}_{\text{std.}}}V_{\text{Cu}_{\text{std.}}}Mr_{CuSO_4 \cdot 5\,H_2O}}
\tag{4.1.8}
$$

Using equations 4.1.1 and 4.1.8 to determine the amount of copper which was exchanged into the zeolite ($n_{\text{Cu}_{\text{ex.}}}$) letting $V_{\text{Cu}_{\text{react.}}}$ be the volume of the standard solution added to the HZSM-5.

$$n_{\text{Cu}_{\text{ex.}}} = [\text{CuSO}_4]V_{\text{Cu}_{\text{react.}}} - n_{\text{Cu}_{\text{prod.}}}$$
$$= \frac{m_{\text{CuSO}_4 \cdot 5\,\text{H}_2\text{O}}V_{\text{Cu}_{\text{react.}}}}{V_{\text{Cu}_{\text{std.}}}Mr_{\text{CuSO}_4 \cdot 5\,\text{H}_2\text{O}}} - \frac{A_{\text{Cu}_{\text{prod.}}}V_{\text{Cu}_{\text{prod.}}}m_{\text{CuSO}_4 \cdot 5\,\text{H}_2\text{O}}}{A_{\text{Cu}_{\text{std.}}}V_{\text{Cu}_{\text{std.}}}Mr_{\text{CuSO}_4 \cdot 5\,\text{H}_2\text{O}}} \quad (4.1.9)$$

into equation 4.2.2 and setting $q = 2$ hence gives:

$$\%\ \text{Cu}^{2+}\ \text{Exchanged} = \frac{2Mr_{\text{HZSM-5 unit cell}}A_{\text{Cu}_{\text{prod.}}}V_{\text{Cu}_{\text{prod.}}}m_{\text{CuSO}_4 \cdot 5\,\text{H}_2\text{O}}}{7.68m_{\text{HZSM-5}}A_{\text{Cu}_{\text{std.}}}V_{\text{Cu}_{\text{std.}}}Mr_{\text{CuSO}_4 \cdot 5\,\text{H}_2\text{O}}} \times 100\ \% \quad (4.1.10)$$

Using 4.1.9 with:

$$Mr_{\text{HZSM-5 unit cell}} = 6217.6134\,\text{g}\,\text{mol}^{-1}\ \text{from equation 4.2.1}$$
$$A_{\text{Cu}_{\text{prod.}}} = 0.110\ \text{from table 2}$$
$$V_{\text{Cu}_{\text{prod.}}} = 100.00 \pm 0.20 \times 10^{-3}\,\text{dm}^3$$
$$m_{\text{CuSO}_4 \cdot 5\,\text{H}_2\text{O}} = 0.501\,40 \pm 0.000\,05\,\text{g}\ \text{from table 1}$$
$$m_{\text{HZSM-5}} = 0.481\,00 \pm 0.000\,05\,\text{g}\ \text{from table 1}$$
$$A_{\text{Cu}_{\text{std.}}} = 0.484\ \text{from table 2}$$
$$V_{\text{Cu}_{\text{std.}}} = 50.00 \pm 0.06 \times 10^{-3}\,\text{dm}^3$$
$$Mr_{\text{CuSO}_4 \cdot 5\,\text{H}_2\text{O}} = 249.577\,\text{g}\,\text{mol}^{-1}\ \text{from equation 4.1.5}$$

$$\%\ \text{Cu}^{2+}\ \text{Exchanged} = \frac{2 \times 6217.6134\,\text{g}\,\text{mol}^{-1} \times 0.00\,\text{mol}}{7.68 \times 0.4810\,\text{g}} \times 100\ \% = 0.00\ \%$$

4.2   Calculations

4.2.1   Calculation of Maximum Theoretical Number of Ion Exchanges

The SiO_2/Al_2O_3 ratio in the zeolite used was 23. In this ratio there are two Al atoms per Si, so $Si/Al = \frac{23}{2} = 11.5$.

Using the unit cell general formula (equation 2.1.1) letting the Si/Al ratio be r and with n being the number of aluminium atoms per unit cell:

$$r = \frac{\text{Number of Si per unit cell}}{\text{Number of Al per unit cell}} = \frac{96 - n}{n}$$
$$nr + n = 96$$
$$\therefore n = \frac{96}{r + 1}$$

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Hence for $r = 11.5$ there are $n = \frac{96}{11.5+1} = 7.68$ Al per unit cell. Letting q be the cation charge and x be the number of water molecules for unit cell:

$$
\begin{aligned}
Mr_{\text{unit cell}} = {} & \frac{7.68}{q} Mr_{\text{cation}} + (11.5(26.982) + (96 - 7.68)(28.085) + 192(15.999) \\
& + x(2(1.008) + 15.999)) \text{g mol}^{-1} \\
= {} & \frac{7.68}{q} Mr_{\text{cation}} + 5759.4692 \,\text{g mol}^{-1} + x(450.375 \,\text{g mol}^{-1})
\end{aligned}
$$

Thus for HZSM-5 where the cation is H$^+$ and $x \approx 25$.[24]

$$
\begin{aligned}
Mr_{\text{HZSM-5 unit cell}} &= \frac{7.68}{1} \times 1.008 \,\text{g mol}^{-1} + (5759.49692 + 25(450.375)) \text{ g mol}^{-1} \\
&= 6217.6134 \,\text{g mol}^{-1}
\end{aligned}
$$

$$(4.2.1)$$

Let: q be the cation charge; $n_{\text{max. cation}}$ be the theoretical maximum amount of cation which can be exchanged and n_{cation}, m_{cation} and Mr_{cation} be the actual amount, mass and Mr of the cation exchanged respectively.

$$
\begin{aligned}
n_{\text{HZSM-5 unit cell}} &= \frac{m_{\text{HZSM-5}}}{Mr_{\text{HZSM-5 unit cell}}} \\
n_{\text{max. cation}} &= \frac{7.68}{q} n_{\text{HZSM-5 unit cell}} \\
&= \frac{7.68}{q} \frac{m_{\text{HZSM-5}}}{Mr_{\text{HZSM-5 unit cell}}} \\
\% \text{ Exchanged} &= \frac{n_{\text{cation}}}{n_{\text{max. cation}}} \times 100\,\% \\
&= \frac{q Mr_{\text{HZSM-5 unit cell}} n_{\text{cation}}}{7.68 m_{\text{HZSM-5}}} \times 100\,\% \qquad (4.2.2)
\end{aligned}
$$

4.2.1.1 Copper

4.3 Copper

For zeolite:

5 Analysis

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6 Supplementary Information