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

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06/03/2018

Abstract

In this project the efficiency of the ion exchange process of HZSM-5 with copper and zinc cations was investigated. The method utilised was found to be ineffective at the completion of this aim and no meaningful conclusions could be drawn from the data collected.

1 Aim

This project aimed to investigate how the efficiency of the ion exchange process is effected by the cation being exchanged. Specifically a comparison between the copper and zinc cation exchange processes of an HZSM-5 zeolite was attempted.

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 140–150° ≈ 180° for silicas and aluminosilicates and the A atoms are represented by the vertices).[7]
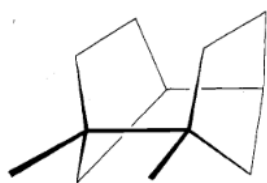

Figure 1: Secondary building unit for ZSM-5 zeolite.[4]

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]
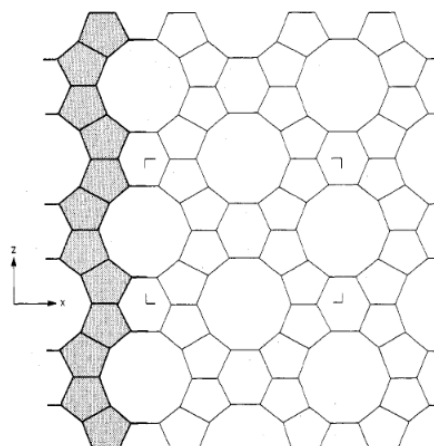

Figure 3: Layer of ZSM-5 zeolite.[4]

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 SiO_2/AlO_3 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

3

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 $20.00\,\mathrm{cm^3}$ aliquots of the zinc solution was titrated against a standard ethylenediaminetetraacetate (EDTA) solution (batch A: $0.4993\,\mathrm{mol\,dm^{-3}}$) with $2\,\mathrm{cm^3}$ of a pH 10 buffer solution and eriochrome black T as the indicator (colour change from red to light blue).

4 Results

4.1 Copper-Exchanged Zeolite

Table 1: Masses used for the preparation of CuZSM-5.

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

The uncertainty in the absorbance values recorded by the spectrophotometer can be modelled using the following equation:[24]

$$\delta Abs = Abs\sqrt{\left(\frac{0.434}{Abs}k_2\sqrt{1+10^{Abs}}\right)^2 + \left(\frac{0.434}{Abs}k_3\right)^2} \qquad (4.1.1)$$

Where k_2 is a measure of the expected precision of the instrument itself for a specific solution and k_3 is a measure of the uncertainty introduced by replacing the cuvette.

Using the values of $k_2 = 4.5 \times 10^{-4}$ and $k_3 = 27 \times 10^{-4}$ recorded by Galbán et al.[24] for the PerkinElmer Lambda 5 spectrophotometer with the ferroin solution since these values produce the largest overall uncertainty, hence giving the most generous reasonable estimate in the uncertainty of the absorbances recorded. Using these values with the

absorbances in table 2 and letting $A_{\text{Cu}_{\text{std.}}}$ be the absorbance of the standard $CuSO_4$ solution and $A_{\text{Cu}_{\text{prod.}}}$ be the absorbance of the post-reaction solution:

$$\delta A_{\text{Cu}_{\text{std.}}} = 0.484\sqrt{\left(\frac{0.434}{0.484} \times 4.5 \times 10^{-4}\sqrt{1 + 10^{0.484}}\right)^2 + \left(\frac{0.434}{0.484} \times 27 \times 10^{-4}\right)^2}$$
$$= 0.001 \qquad\qquad (4.1.2)$$

$$\delta A_{\text{Cu}_{\text{prod.}}} = 0.110\sqrt{\left(\frac{0.434}{0.110} \times 4.5 \times 10^{-4}\sqrt{1 + 10^{0.110}}\right)^2 + \left(\frac{0.434}{0.110} \times 27 \times 10^{-4}\right)^2}$$
$$= 0.001 \qquad\qquad (4.1.3)$$

4.2 Zinc-Exchanged Zeolite

Table 3: Masses used in preparation of the $ZnSO_4$ standard solution utilised in the standardisation of the EDTA solution.

Substance	Mass / g
$ZnSO_4 \cdot 7\,H_2O$	0.4587

Table 4: Masses used for the preparation of ZnZSM-5.

Substance	Mass / g
$ZnSO_4 \cdot 7\,H_2O$	0.6331
HZSM-5	0.5274

The reaction which occurred during the titrations between the $EDTA^{4-}$ and Zn^{2+} ions in given in equation 4.2.1.

$$Zn^{2+}\,(aq) + EDTA^{4-}\,(aq) \longrightarrow ZnEDTA^{2-}\,(aq) \qquad\qquad (4.2.1)$$

Due to time constraints the standardisation of the EDTA solution was not fully completed, hence the accurate titre volume ($V_{\text{EDTA}_{\text{std.}}}$) has been assumed to be the titre volume from the second titre (see table 5) in the absence of additional available titrations to confirm this.

Table 5: Titration results from standardisation of EDTA solution with standard zinc sulphate solution.

Run	Start Volume / cm^3	End Volume / cm^3	Titre Volume / cm^3
1	1.45	33.70	32.25
2	2.25	34.20	31.95

Table 6: Titration results between zinc solution after ion-exchange process and standardised EDTA solution.

Run	Start Volume / cm^3	End Volume / cm^3	Titre Volume / cm^3
1	2.40	29.10	26.70
2	2.90	29.55	26.65
3	1.40	28.00	26.60
4	11.35	37.70	26.35

$$V_{\text{EDTA}_{std.}} = 31.95 \, \text{cm}^3 \tag{4.2.2}$$

The average titre volume for the titration with the post ion-exchange solution ($V_{\text{EDTA}_{\text{prod.}}}$) was determined from the second and third runs (see table 6) since the first run was a rough titration and the fourth run can be clearly seen be be anomalous.

$$V_{\text{EDTA}_{\text{prod.}}} = \frac{26.65 \, \text{cm}^3 + 26.60 \, \text{cm}^3}{2} = 20.63 \, \text{cm}^3 \tag{4.2.3}$$

5 Calculations

5.1 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:

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

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:

$$Mr_{\text{unit cell}} = \frac{7.68}{q} Mr_{\text{cation}} + (11.5(26.982) + (96 - 7.68)(28.085) + 192(15.999)$$
$$+ x(2(1.008) + 15.999))\text{g mol}^{-1}$$
$$= \frac{7.68}{q} Mr_{\text{cation}} + 5759.469 \, \text{g mol}^{-1} + x(450.375 \, \text{g mol}^{-1})$$

6

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

$$Mr_{\text{HZSM-5 unit cell}} = \frac{7.68}{1} \times 1.008 \, \text{g mol}^{-1} + (5759.469 + 25(450.375)) \, \text{g mol}^{-1}$$
$$= 6217.613 \, \text{g mol}^{-1} \tag{5.1.1}$$

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.

$$n_{\text{HZSM-5 unit cell}} = \frac{m_{\text{HZSM-5}}}{Mr_{\text{HZSM-5 unit cell}}}$$
$$n_{\text{max. cation}} = \frac{7.68}{q} n_{\text{HZSM-5 unit cell}}$$
$$= \frac{7.68}{q} \frac{m_{\text{HZSM-5}}}{Mr_{\text{HZSM-5 unit cell}}}$$
$$\% \text{ Exchanged} = \frac{n_{\text{cation}}}{n_{\text{max. cation}}} \times 100\,\%$$
$$= \frac{q Mr_{\text{HZSM-5 unit cell}} n_{\text{cation}}}{7.68 m_{\text{HZSM-5}}} \times 100\,\% \tag{5.1.2}$$

5.2 Calculations for Copper Solution

5.2.1 Determination of Molar Extinction Coefficient

Let $V_{\text{Cu}_{\text{std.}}}$ be the volume and $[\text{CuSO}_4]_{\text{std.}}$ be the concentration of the standard Cu^{2+} solution.

$$n_{\text{CuSO}_4} = \frac{m_{\text{CuSO}_4 \cdot 5\,H_2O}}{Mr_{\text{CuSO}_4 \cdot 5\,H_2O}}$$
$$[\text{CuSO}_4]_{\text{std.}} = \frac{n_{\text{CuSO}_4}}{V_{\text{Cu}_{\text{std.}}}}$$
$$= \frac{m_{\text{CuSO}_4 \cdot 5\,H_2O}}{V_{\text{Cu}_{\text{std.}}} Mr_{\text{CuSO}_4 \cdot 5\,H_2O}} \tag{5.2.1}$$

Rearranging the Beer-Lambert law (equation 5.2.2) for the molar extinction coefficient:

$$A = \epsilon c l \tag{5.2.2}$$
$$\epsilon = \frac{A}{cl} \tag{5.2.3}$$

Hence using equations 5.2.1 and 5.2.3:

$$\begin{aligned}
\epsilon_{\mathrm{CuSO_4}} &= \frac{A_{\mathrm{Cu_{std.}}}}{[\mathrm{CuSO_4}]_{\mathrm{std.}}\, l} \\
&= \frac{A_{\mathrm{Cu_{std.}}}\, V_{\mathrm{Cu_{std.}}}\, Mr_{\mathrm{CuSO_4 \cdot 5\,H_2O}}}{l\, m_{\mathrm{CuSO_4 \cdot 5\,H_2O}}}
\end{aligned} \tag{5.2.4}$$

5.2.2 Determination of $\mathrm{Cu^{2+}}$ Ion-Exchange Level

By rearranging the Beer-Lambert Law (equation 5.2.2) for concentration:

$$c = \frac{A}{\epsilon l} \tag{5.2.5}$$

Letting $[\mathrm{CuSO_4}]_{\mathrm{prod.}}$ be the concentration, $n_{\mathrm{Cu_{prod.}}}$ be the amount of $\mathrm{Cu^{2+}}$ ions and $V_{\mathrm{Cu_{prod.}}}$ be the volume of the solution after the ion-exchange reaction while using equation 5.2.5:

$$\begin{aligned}
[\mathrm{CuSO_4}]_{\mathrm{prod.}} &= \frac{A_{\mathrm{Cu_{prod.}}}}{\epsilon_{\mathrm{CuSO_4}} l} \\
n_{\mathrm{Cu_{prod.}}} &= [\mathrm{CuSO_4}]_{\mathrm{prod.}} V_{\mathrm{Cu_{prod.}}} \\
&= \frac{A_{\mathrm{Cu_{prod.}}}\, V_{\mathrm{Cu_{prod.}}}}{\epsilon_{\mathrm{CuSO_4}} l}
\end{aligned} \tag{5.2.6}$$

Substituting equation 5.2.4 into 5.2.6:

$$n_{\mathrm{Cu_{prod.}}} = \frac{A_{\mathrm{Cu_{prod.}}}\, V_{\mathrm{Cu_{prod.}}}\, m_{\mathrm{CuSO_4 \cdot 5\,H_2O}}}{A_{\mathrm{Cu_{std.}}}\, V_{\mathrm{Cu_{std.}}}\, Mr_{\mathrm{CuSO_4 \cdot 5\,H_2O}}} \tag{5.2.7}$$

Using equations 5.2.1 and 5.2.7 to determine the amount of copper which was exchanged into the zeolite ($n_{\mathrm{Cu_{ex.}}}$) letting $V_{\mathrm{Cu_{react.}}}$ be the volume of the standard solution added to the HZSM-5.

$$\begin{aligned}
n_{\mathrm{Cu_{ex.}}} &= [\mathrm{CuSO_4}] V_{\mathrm{Cu_{react.}}} - n_{\mathrm{Cu_{prod.}}} \\
&= \frac{m_{\mathrm{CuSO_4 \cdot 5\,H_2O}} V_{\mathrm{Cu_{react.}}}}{V_{\mathrm{Cu_{std.}}}\, Mr_{\mathrm{CuSO_4 \cdot 5\,H_2O}}} - \frac{A_{\mathrm{Cu_{prod.}}}\, V_{\mathrm{Cu_{prod.}}}\, m_{\mathrm{CuSO_4 \cdot 5\,H_2O}}}{A_{\mathrm{Cu_{std.}}}\, V_{\mathrm{Cu_{std.}}}\, Mr_{\mathrm{CuSO_4 \cdot 5\,H_2O}}} \\
&= \frac{m_{\mathrm{CuSO_4 \cdot 5\,H_2O}} \left(A_{\mathrm{Cu_{std.}}}\, V_{\mathrm{Cu_{react.}}} - A_{\mathrm{Cu_{prod.}}}\, V_{\mathrm{Cu_{prod.}}} \right)}{A_{\mathrm{Cu_{std.}}}\, V_{\mathrm{Cu_{std.}}}\, Mr_{\mathrm{CuSO_4 \cdot 5\,H_2O}}}
\end{aligned} \tag{5.2.8}$$

Substituting equation 5.2.8 into equation 5.1.2 and setting $q = 2$ hence gives:

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

$$(5.2.9)$$

Using 5.2.9 with:

$$Mr_{\text{HZSM-5 unit cell}} = 6217.613\,\text{g mol}^{-1} \text{ from equation 5.1.1}$$
$$m_{\text{CuSO}_4 \cdot 5\,\text{H}_2\text{O}} = 0.501\,40 \pm 0.000\,05\,\text{g from table 1}$$
$$A_{\text{Cu}_{\text{std.}}} = 0.484 \pm 0.001 \text{ from table 2 and equation 4.1.2}$$
$$V_{\text{Cu}_{\text{react.}}} = 20.00 \pm 0.06 \times 10^{-3}\,\text{dm}^3 \text{ from method (section 3)}$$
$$A_{\text{Cu}_{\text{prod.}}} = 0.110 \pm 0.001 \text{ from table 2 and equation 4.1.3}$$
$$V_{\text{Cu}_{\text{prod.}}} = 100.00 \pm 0.20 \times 10^{-3}\,\text{dm}^3 \text{ from method (section 3)}$$
$$m_{\text{HZSM-5}} = 0.481\,00 \pm 0.000\,05\,\text{g from table 1}$$
$$V_{\text{Cu}_{\text{std.}}} = 50.00 \pm 0.06 \times 10^{-3}\,\text{dm}^3 \text{ from method (section 3)}$$
$$Mr_{\text{CuSO}_4 \cdot 5\,\text{H}_2\text{O}} = 249.685\,\text{g mol}^{-1}{}^{26}$$

$$\% \text{ Cu}^{2+} \text{ Exchanged} = \frac{2 \times 6217.613\,\text{g mol}^{-1} \times 0.501\,40\,\text{g}\,(0.484 \times 20.00 - 0.110 \times 100.00)\,10^{-3}\,\text{dm}^3}{7.68 \times 0.4810\,\text{g} \times 0.484 \times 50.00 \times 10^{-3}\,\text{dm}^3 \times 249.577\,\text{g mol}^{-1}}$$
$$\times 100\,\%$$
$$= -37\,\%$$

5.2.3   Error Propagation

Let the percentage of Cu^{2+} exchanged be v_{Cu} in the error propagation below:

$$\delta v_{\text{Cu}} = v_{\text{Cu}} \left(\left(\frac{\delta Mr_{\text{HZSM-5 unit cell}}}{Mr_{\text{HZSM-5 unit cell}}} \right)^2 + \left(\frac{\delta m_{\text{CuSO}_4 \cdot 5\,\text{H}_2\text{O}}}{m_{\text{CuSO}_4 \cdot 5\,\text{H}_2\text{O}}} \right)^2 + \left(\frac{\delta \left(A_{\text{Cu}_{\text{std.}}} V_{\text{Cu}_{\text{react.}}} - A_{\text{Cu}_{\text{prod.}}} V_{\text{Cu}_{\text{prod.}}} \right)}{A_{\text{Cu}_{\text{std.}}} V_{\text{Cu}_{\text{react.}}} - A_{\text{Cu}_{\text{prod.}}} V_{\text{Cu}_{\text{prod.}}}} \right)^2 \right.$$

$$\left. + \left(\frac{\delta m_{\text{HZSM-5}}}{m_{\text{HZSM-5}}} \right)^2 + \left(\frac{\delta A_{\text{Cu}_{\text{std.}}}}{A_{\text{Cu}_{\text{std.}}}} \right)^2 + \left(\frac{\delta V_{\text{Cu}_{\text{std.}}}}{V_{\text{Cu}_{\text{std.}}}} \right)^2 + \left(\frac{\delta Mr_{\text{CuSO}_4 \cdot 5\,\text{H}_2\text{O}}}{Mr_{\text{CuSO}_4 \cdot 5\,\text{H}_2\text{O}}} \right)^2 \right)^{1/2}$$

$$(5.2.10)$$

Let $S = A_{\text{Cu}_{\text{std.}}} V_{\text{Cu}_{\text{react.}}} - A_{\text{Cu}_{\text{prod.}}} V_{\text{Cu}_{\text{prod.}}}$, thus:

$$
\begin{aligned}
\delta S &= \left(\left(\delta \left(A_{\text{Cu}_{\text{std.}}} V_{\text{Cu}_{\text{react.}}} \right) \right)^2 + \left(\delta \left(A_{\text{Cu}_{\text{prod.}}} V_{\text{Cu}_{\text{prod.}}} \right) \right)^2 \right)^{1/2} \\
&= \left(\left(A_{\text{Cu}_{\text{std.}}} V_{\text{Cu}_{\text{react.}}} \left(\left(\frac{\delta A_{\text{Cu}_{\text{std.}}}}{A_{\text{Cu}_{\text{std.}}}} \right)^2 + \left(\frac{\delta V_{\text{Cu}_{\text{react.}}}}{V_{\text{Cu}_{\text{react.}}}} \right)^2 \right)^{1/2} \right)^2 \right. \\
&\quad + \left. \left(A_{\text{Cu}_{\text{prod.}}} V_{\text{Cu}_{\text{prod.}}} \left(\left(\frac{\delta A_{\text{Cu}_{\text{prod.}}}}{A_{\text{Cu}_{\text{prod.}}}} \right)^2 + \left(\frac{\delta V_{\text{Cu}_{\text{prod.}}}}{V_{\text{Cu}_{\text{prod.}}}} \right)^2 \right)^{1/2} \right)^2 \right)^{1/2} \\
&= \left(A_{\text{Cu}_{\text{std.}}}^2 V_{\text{Cu}_{\text{react.}}}^2 \left(\left(\frac{\delta A_{\text{Cu}_{\text{std.}}}}{A_{\text{Cu}_{\text{std.}}}} \right)^2 + \left(\frac{\delta V_{\text{Cu}_{\text{react.}}}}{V_{\text{Cu}_{\text{react.}}}} \right)^2 \right) \right. \\
&\quad + \left. A_{\text{Cu}_{\text{prod.}}}^2 V_{\text{Cu}_{\text{prod.}}}^2 \left(\left(\frac{\delta A_{\text{Cu}_{\text{prod.}}}}{A_{\text{Cu}_{\text{prod.}}}} \right)^2 + \left(\frac{\delta V_{\text{Cu}_{\text{prod.}}}}{V_{\text{Cu}_{\text{prod.}}}} \right)^2 \right) \right)^{1/2}
\end{aligned}
\tag{5.2.11}
$$

Hence substituting equation 5.2.11 into 5.2.10 gives:

$$
\begin{aligned}
\delta v_{\text{Cu}} = v_{\text{Cu}} \left(\right. & \left(\frac{\delta Mr_{\text{HZSM-5 unit cell}}}{Mr_{\text{HZSM-5 unit cell}}} \right)^2 + \left(\frac{\delta m_{\text{CuSO}_4 \cdot 5\,\text{H}_2\text{O}}}{m_{\text{CuSO}_4 \cdot 5\,\text{H}_2\text{O}}} \right)^2 \\
& + \frac{A_{\text{Cu}_{\text{std.}}}^2 V_{\text{Cu}_{\text{react.}}}^2 \left(\left(\frac{\delta A_{\text{Cu}_{\text{std.}}}}{A_{\text{Cu}_{\text{std.}}}} \right)^2 + \left(\frac{\delta V_{\text{Cu}_{\text{react.}}}}{V_{\text{Cu}_{\text{react.}}}} \right)^2 \right) + A_{\text{Cu}_{\text{prod.}}}^2 V_{\text{Cu}_{\text{prod.}}}^2 \left(\left(\frac{\delta A_{\text{Cu}_{\text{prod.}}}}{A_{\text{Cu}_{\text{prod.}}}} \right)^2 + \left(\frac{\delta V_{\text{Cu}_{\text{prod.}}}}{V_{\text{Cu}_{\text{prod.}}}} \right)^2 \right)}{\left(A_{\text{Cu}_{\text{std.}}} V_{\text{Cu}_{\text{react.}}} - A_{\text{Cu}_{\text{prod.}}} V_{\text{Cu}_{\text{prod.}}} \right)^2} \\
& + \left(\frac{\delta m_{\text{HZSM-5}}}{m_{\text{HZSM-5}}} \right)^2 + \left(\frac{\delta A_{\text{Cu}_{\text{std.}}}}{A_{\text{Cu}_{\text{std.}}}} \right)^2 + \left(\frac{\delta V_{\text{Cu}_{\text{std.}}}}{V_{\text{Cu}_{\text{std.}}}} \right)^2 + \left(\frac{\delta Mr_{\text{CuSO}_4 \cdot 5\,\text{H}_2\text{O}}}{Mr_{\text{CuSO}_4 \cdot 5\,\text{H}_2\text{O}}} \right)^2 \left. \right)^{1/2}
\end{aligned}
\tag{5.2.12}
$$

Substituting values into equation 5.2.12 thus yields:

$$
\delta v_{\text{Cu}} = \pm 3\,\%
$$

So the percentage of Cu^{2+} exchanged is $-37 \pm 3\,\%$.

5.3   Calculations for Zinc Solution

5.3.1   Determination of EDTA Solution (Batch A) Concentration

Letting $V_{Zn_{std.}}$ be the volume, $[ZnSO_4]_{std.}$ be the concentration and $m_{ZnSO_4 \cdot 7\,H_2O_{std.}}$ be the mass of $ZnSO_4 \cdot 7\,H_2O$ used for the preparation of the $ZnSO_4$ standard solution used to standardise the EDTA solution.

$$[ZnSO_4]_{std.} = \frac{m_{ZnSO_4 \cdot 7\,H_2O_{std.}}}{Mr_{ZnSO_4 \cdot 7\,H_2O}V_{Zn_{std.}}} \tag{5.3.1}$$

From equation 4.2.1 there is a 1:1 stoichiometric ratio between the Zn^{2+} and $EDTA^{4-}$ ions hence letting $[EDTA^{4-}]$ be the concentration of the EDTA solution $n_{Zn_{std.\ analyte}}$ be the amount and $V_{Zn_{std.\ aliquot}}$ be the volume of Zn^{2+} ions in the analyte.

$$[EDTA^{4-}] = \frac{n_{Zn_{std.\ analyte}}}{V_{EDTA_{std.}}} = \frac{[ZnSO_4]_{std.}V_{Zn_{std.\ aliquot}}}{V_{EDTA_{std.}}} \tag{5.3.2}$$

Thus substituting equation 5.3.1 into equation 5.3.2 gives:

$$[EDTA^{4-}] = \frac{m_{ZnSO_4 \cdot 7\,H_2O_{std.}}V_{Zn_{std.\ aliquot}}}{Mr_{ZnSO_4 \cdot 7\,H_2O}V_{Zn_{std.}}V_{EDTA_{std.}}} \tag{5.3.3}$$

5.3.2   Determination of Zn^{2+} Ion Exchange Level

Let $[ZnSO_4]_{std.\ orig.}$ be the concentration of, $m_{ZnSO_4 \cdot 7\,H_2O_{orig.}}$ be the mass of zinc sulphate used and $V_{Zn_{std.\ orig.}}$ be the volume of the standard zinc sulphate solution created for the ion exchange process.

$$[ZnSO_4]_{std.\ orig.} = \frac{m_{ZnSO_4 \cdot 7\,H_2O_{orig.}}}{Mr_{ZnSO_4 \cdot 7\,H_2O}V_{Zn_{std.\ orig.}}} \tag{5.3.4}$$

Using equation 5.3.4 with $V_{Zn_{orig.}}$ as the volume of the stanadard solution used in the ion-exchange process.

$$\begin{aligned}
n_{Zn_{orig.}} &= [ZnSO_4]_{std.\ orig.}V_{Zn_{orig.}} \\
&= \frac{m_{ZnSO_4 \cdot 7\,H_2O_{orig.}}V_{Zn_{orig.}}}{Mr_{ZnSO_4 \cdot 7\,H_2O}V_{Zn_{std.\ orig.}}}
\end{aligned} \tag{5.3.5}$$

Using equation 5.3.3 the amount of zinc remaining in solution after the ion-exchange ($n_{\text{Zn}_{\text{prod.}}}$) can be calculated with $V_{\text{Zn}_{\text{prod.}}}$ being the volume of this resultant solution and $V_{\text{Zn}_{\text{prod. aliquot}}}$ being the volume of the aliquot titrated.

$$
\begin{aligned}
n_{\text{Zn}_{\text{prod.}}} &= \frac{V_{\text{EDTA}_{\text{prod.}}}[\text{EDTA}^{4-}]V_{\text{Zn}_{\text{prod.}}}}{V_{\text{Zn}_{\text{prod. aliquot}}}} \\
&= \frac{V_{\text{EDTA}_{\text{prod.}}}m_{\text{ZnSO}_4\cdot 7\,\text{H}_2\text{O}_{\text{std.}}}V_{\text{Zn}_{\text{std. aliquot}}}V_{\text{Zn}_{\text{prod.}}}}{V_{\text{Zn}_{\text{prod. aliquot}}}Mr_{\text{ZnSO}_4\cdot 7\,\text{H}_2\text{O}}V_{\text{Zn}_{\text{std.}}}V_{\text{EDTA}_{\text{std.}}}}
\end{aligned}
\tag{5.3.6}
$$

Using equations 5.3.5 and 5.3.6 to calculate the amount of Zn^{2+} ions exchanged with the HZSM-5 ($n_{\text{Zn}_{\text{ex.}}}$):

$$
\begin{aligned}
n_{\text{Zn}_{\text{ex.}}} &= n_{\text{Zn}_{\text{orig.}}} - n_{\text{Zn}_{\text{prod.}}} \\
&= \frac{m_{\text{ZnSO}_4\cdot 7\,\text{H}_2\text{O}_{\text{orig.}}}V_{\text{Zn}_{\text{orig.}}}}{Mr_{\text{ZnSO}_4\cdot 7\,\text{H}_2\text{O}}V_{\text{Zn}_{\text{std. orig.}}}} - \frac{V_{\text{EDTA}_{\text{prod.}}}m_{\text{ZnSO}_4\cdot 7\,\text{H}_2\text{O}_{\text{std.}}}V_{\text{Zn}_{\text{std. aliquot}}}V_{\text{Zn}_{\text{prod.}}}}{V_{\text{Zn}_{\text{prod. aliquot}}}Mr_{\text{ZnSO}_4\cdot 7\,\text{H}_2\text{O}}V_{\text{Zn}_{\text{std.}}}V_{\text{EDTA}_{\text{std.}}}} \\
&= \frac{V_{\text{Zn}_{\text{prod. aliquot}}}V_{\text{Zn}_{\text{std.}}}V_{\text{EDTA}_{\text{std.}}}m_{\text{ZnSO}_4\cdot 7\,\text{H}_2\text{O}_{\text{orig.}}}V_{\text{Zn}_{\text{orig.}}}}{V_{\text{Zn}_{\text{std. orig.}}}V_{\text{Zn}_{\text{prod. aliquot}}}Mr_{\text{ZnSO}_4\cdot 7\,\text{H}_2\text{O}}V_{\text{Zn}_{\text{std.}}}V_{\text{EDTA}_{\text{std.}}}} \\
&\quad - \frac{V_{\text{Zn}_{\text{std. orig.}}}V_{\text{EDTA}_{\text{prod.}}}m_{\text{ZnSO}_4\cdot 7\,\text{H}_2\text{O}_{\text{std.}}}V_{\text{Zn}_{\text{std. aliquot}}}V_{\text{Zn}_{\text{prod.}}}}{V_{\text{Zn}_{\text{std. orig.}}}V_{\text{Zn}_{\text{prod. aliquot}}}Mr_{\text{ZnSO}_4\cdot 7\,\text{H}_2\text{O}}V_{\text{Zn}_{\text{std.}}}V_{\text{EDTA}_{\text{std.}}}}
\end{aligned}
\tag{5.3.7}
$$

Hence substituting equation 5.3.7 into 5.1.2 and setting $q = 2$ gives:

$$
\begin{aligned}
\% \text{ Zn Exchanged} &= \frac{2Mr_{\text{HZSM-5 unit cell}}}{7.68 m_{\text{HZSM-5}}V_{\text{Zn}_{\text{std. orig.}}}V_{\text{Zn}_{\text{prod. aliquot}}}Mr_{\text{ZnSO}_4\cdot 7\,\text{H}_2\text{O}}V_{\text{Zn}_{\text{std.}}}V_{\text{EDTA}_{\text{std.}}}} \\
&\quad \times (V_{\text{Zn}_{\text{prod. aliquot}}}V_{\text{Zn}_{\text{std.}}}V_{\text{EDTA}_{\text{std.}}}m_{\text{ZnSO}_4\cdot 7\,\text{H}_2\text{O}_{\text{orig.}}}V_{\text{Zn}_{\text{orig.}}} \\
&\quad - V_{\text{Zn}_{\text{std. orig.}}}V_{\text{EDTA}_{\text{prod.}}}m_{\text{ZnSO}_4\cdot 7\,\text{H}_2\text{O}_{\text{std.}}}V_{\text{Zn}_{\text{std. aliquot}}}V_{\text{Zn}_{\text{prod.}}}) \times 100\,\%
\end{aligned}
\tag{5.3.8}
$$

Using equation 5.3.8 with:

$$Mr_{\text{HZSM-5 unit cell}} = 6217.613\,\text{g mol}^{-1} \text{ from equation 5.1.1}$$

$$V_{\text{Zn}_{\text{prod. aliquot}}} = 20.00 \pm 0.06 \times 10^{-3}\,\text{dm}^3 \text{ from method (section 3)}$$

$$V_{\text{Zn}_{\text{std.}}} = 100.00 \pm 0.20 \times 10^{-3}\,\text{dm}^3 \text{ from method (section 3)}$$

$$V_{\text{EDTA}_{\text{std.}}} = 31.95 \pm 0.20 \times 10^{-3}\,\text{dm}^3 \text{ from equation 4.2.2}$$

$$m_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}_{\text{orig.}}} = 0.633\,10 \pm 0.000\,05 \times 10^{-3}\,\text{g from table 4}$$

$$V_{\text{Zn}_{\text{orig.}}} = 20.00 \pm 0.06 \times 10^{-3}\,\text{dm}^3 \text{ from method (section 3)}$$

$$V_{\text{Zn}_{\text{std. orig.}}} = 50.00 \pm 0.06 \times 10^{-3}\,\text{dm}^3 \text{ from method (section 3)}$$

$$V_{\text{EDTA}_{\text{prod.}}} = 26.63 \pm 0.20 \times 10^{-3}\,\text{dm}^3 \text{ from equation 4.2.3}$$

$$m_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}_{\text{std.}}} = 0.458\,70 \pm 0.000\,05\,\text{g from table 3}$$

$$V_{\text{Zn}_{\text{std. aliquot}}} = 10.00 \pm 0.04 \times 10^{-3}\,\text{dm}^3 \text{ from method (section 3)}$$

$$V_{\text{Zn}_{\text{prod.}}} = 100.00 \pm 0.20 \times 10^{-3}\,\text{dm}^3 \text{ from method (section 3)}$$

$$m_{\text{HZSM-5}} = 0.527\,40 \pm 0.000\,05\,\text{g from table 4}$$

$$Mr_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}} = 287.578\,\text{g mol}^{-1}{}^{26}$$

Gives:

$$\% \text{ Zn Exchanged} = 66\,\%$$

5.3.3 Error Propagation

Let the percentage of Zn^{2+} exchanged be v_{Zn} in the following error propagation:

$$
\begin{aligned}
\delta v_{\text{Zn}} =& v_{\text{Zn}} \Bigg(\left(\frac{\delta Mr_{\text{HZSM-5 unit cell}}}{Mr_{\text{HZSM-5 unit cell}}} \right)^2 + \left(\frac{\delta m_{\text{HZSM-5}}}{m_{\text{HZSM-5}}} \right)^2 + \left(\frac{\delta V_{\text{Zn}_{\text{std. orig.}}}}{V_{\text{Zn}_{\text{std. orig.}}}} \right)^2 + \left(\frac{\delta V_{\text{Zn}_{\text{prod. aliquot}}}}{V_{\text{Zn}_{\text{prod. aliquot}}}} \right)^2 \\
&+ \left(\frac{\delta Mr_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}}}{Mr_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}}} \right)^2 + \left(\frac{\delta V_{\text{Zn}_{\text{std.}}}}{V_{\text{Zn}_{\text{std.}}}} \right)^2 + \left(\frac{\delta V_{\text{EDTA}_{\text{std.}}}}{V_{\text{EDTA}_{\text{std.}}}} \right)^2 \\
&+ \Bigg(\frac{\delta\big(V_{\text{Zn}_{\text{prod. aliquot}}} V_{\text{Zn}_{\text{std.}}} V_{\text{EDTA}_{\text{std.}}} m_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}_{\text{orig.}}} V_{\text{Zn}_{\text{orig.}}} - V_{\text{Zn}_{\text{std. orig.}}} V_{\text{EDTA}_{\text{prod.}}} m_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}_{\text{std.}}} }{V_{\text{Zn}_{\text{prod. aliquot}}} V_{\text{Zn}_{\text{std.}}} V_{\text{EDTA}_{\text{std.}}} m_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}_{\text{orig.}}} V_{\text{Zn}_{\text{orig.}}} - V_{\text{Zn}_{\text{std. orig.}}} V_{\text{EDTA}_{\text{prod.}}} m_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}_{\text{std.}}} } \\
&\quad \frac{V_{\text{Zn}_{\text{std. aliquot}}} V_{\text{Zn}_{\text{prod.}}}\big)}{V_{\text{Zn}_{\text{std. aliquot}}} V_{\text{Zn}_{\text{prod.}}}} \Bigg)^2 \Bigg)^{1/2}
\end{aligned}
$$

$$(5.3.9)$$

Using the same method demonstrated in section 5.2.3 in equation 5.2.11 to expand equation 5.3.9 hence gives:

$$
\begin{aligned}
\delta v_{\mathrm{Zn}} = v_{\mathrm{Zn}} &\left(\left(\frac{\delta Mr_{\text{HZSM-5 unit cell}}}{Mr_{\text{HZSM-5 unit cell}}} \right)^2 + \left(\frac{\delta m_{\text{HZSM-5}}}{m_{\text{HZSM-5}}} \right)^2 + \left(\frac{\delta V_{\mathrm{Zn_{std.\ orig.}}}}{V_{\mathrm{Zn_{std.\ orig.}}}} \right)^2 + \left(\frac{\delta V_{\mathrm{Zn_{prod.\ aliquot}}}}{V_{\mathrm{Zn_{prod.\ aliquot}}}} \right)^2 \right. \\[2ex]
&+ \left(\frac{\delta Mr_{\mathrm{ZnSO_4\cdot 7\,H_2O}}}{Mr_{\mathrm{ZnSO_4\cdot 7\,H_2O}}} \right)^2 + \left(\frac{\delta V_{\mathrm{Zn_{std.}}}}{V_{\mathrm{Zn_{std.}}}} \right)^2 + \left(\frac{\delta V_{\mathrm{EDTA_{std.}}}}{V_{\mathrm{EDTA_{std.}}}} \right)^2 \\[2ex]
&+ \frac{V_{\mathrm{Zn_{prod.\ aliquot}}}^2 V_{\mathrm{Zn_{std.}}}^2 V_{\mathrm{EDTA_{std.}}}^2 m_{\mathrm{ZnSO_4\cdot 7\,H_2O_{orig.}}}^2 V_{\mathrm{Zn_{orig.}}}^2 \left(\left(\frac{\delta V_{\mathrm{Zn_{prod.\ aliquot}}}}{V_{\mathrm{Zn_{prod.\ aliquot}}}} \right)^2 + \left(\frac{\delta V_{\mathrm{Zn_{std.}}}}{V_{\mathrm{Zn_{std.}}}} \right)^2 \right.}{\left(V_{\mathrm{Zn_{prod.\ aliquot}}} V_{\mathrm{Zn_{std.}}} V_{\mathrm{EDTA_{std.}}} m_{\mathrm{ZnSO_4\cdot 7\,H_2O_{orig.}}} V_{\mathrm{Zn_{orig.}}} - V_{\mathrm{Zn_{std.\ orig.}}} V_{\mathrm{EDTA_{prod.}}} m_{\mathrm{ZnSO_4\cdot 7\,H_2O_{std.}}}} \\[2ex]
&\qquad \frac{\left. + \left(\frac{\delta V_{\mathrm{EDTA_{std.}}}}{V_{\mathrm{EDTA_{std.}}}} \right)^2 + \left(\frac{\delta m_{\mathrm{ZnSO_4\cdot 7\,H_2O_{orig.}}}}{m_{\mathrm{ZnSO_4\cdot 7\,H_2O_{orig.}}}} \right)^2 + \left(\frac{\delta V_{\mathrm{Zn_{orig.}}}}{V_{\mathrm{Zn_{orig.}}}} \right)^2 \right) + V_{\mathrm{Zn_{std.\ orig.}}}^2 V_{\mathrm{EDTA_{prod.}}}^2 m_{\mathrm{ZnSO_4\cdot 7\,H_2O_{std.}}}^2}{V_{\mathrm{Zn_{std.\ aliquot}}} V_{\mathrm{Zn_{prod.}}} \big)^2} \\[2ex]
&\frac{V_{\mathrm{Zn_{std.\ aliquot}}}^2 V_{\mathrm{Zn_{prod.}}}^2 \left(\left(\frac{\delta V_{\mathrm{Zn_{std.\ orig.}}}}{V_{\mathrm{Zn_{std.\ orig.}}}} \right)^2 + \left(\frac{\delta V_{\mathrm{EDTA_{prod.}}}}{V_{\mathrm{EDTA_{prod.}}}} \right)^2 + \left(\frac{\delta m_{\mathrm{ZnSO_4\cdot 7\,H_2O_{std.}}}}{m_{\mathrm{ZnSO_4\cdot 7\,H_2O_{std.}}}} \right)^2 + \left(\frac{\delta V_{\mathrm{Zn_{std.\ aliquot}}}}{V_{\mathrm{Zn_{std.\ aliquot}}}} \right)^2 \right.}{} \\[2ex]
&\left. \left. \frac{+ \left(\frac{\delta V_{\mathrm{Zn_{prod.}}}}{V_{\mathrm{Zn_{prod.}}}} \right)^2 \right)}{} \right)^{1/2}
\end{aligned}
$$

<div align="right">(5.3.10)</div>

Substituting values into equation 5.3.10 gives:

$$
\delta v_{\mathrm{Zn}} = \pm 3\,\%
$$

Hence the percentage of $\mathrm{Zn^{2+}}$ exchanged is $66 \pm 3\,\%$.

6 Analysis

6.1 General

Between laboratory sessions the solutions were stored in a fridge in an attempt to reduce the rate of ion exchange since some of the ZSM-5 had already been separated out of the copper solution. This is not likely to have been very effective since the temperature of the fridge is still fairly high and the samples were left for a long period of time (one week), hence both samples are likely to have reached new equilibriums during this time thus effecting the results collected. It would have been better if the initial centrifugation of the copper solution was not completed since then both mixtures would have been exposed to the same conditions, hence allowing direct comparison of the ion exchange results.

Losses in the non-exchanged ions are likely to have occurred for both solutions during the centrifugation process since some metal ions will have remained within the precipitate and in the tube when the supernatant fluid was collected. To reduce this loss distilled water could be added to the centrifuge tube and additional centrifugations performed, hence washing the tubes. This was not completed due to time constraints.

Both the copper and zinc solutions were cloudy following the centrifugation indicating that some ZSM-5 remained suspended in the solutions. Further centrifugations wold have reduced the amount of suspended zeolite from the solutions and hence the errors resultant from this (see below). Centrifugation was chosen instead of filtration to separate the zeolite since the nano-size particles of ZSM-5 can block the filter paper during filtrations hence resulting in very long filtration times.[27]

While monomeric species such as Cu^{2+} and Zn^{2+} are likely to be the predominant species present in the ZSM-5 zeolite after the ion exchange process other species such as ($[ZnOH]^+$ which subsequently form $[ZnOZn]^{2+}$ dimeric bridges upon drying) and $[Cu_2(OH)_2]^{2+}$ may alternatively be formed.[28–30] The formation of these species allows a 1:1 exchange between the hydrogen and the metal cations thus enabling an ion exchange level greater than that calculated,[28,29] however the exchange of the monomeric species is the preferred thermodynamic product and the other species only form at isolated Al centres when using aqueous phase ion exchange as the preparation technique.[31,32] It is thus unlikely that a large amount of the dimeric species was present in the products created.

6.2 Copper Exchanged ZSM-5

As seen in section 5.2.1 the calculated exchange level for the Cu^{2+} ions with the HZSM-5 was negative. This can be explained by the presence of the suspended ZSM-5 in solution whichincreased the absorbance value of the sample over the true value thus resulting in the negative yield calculated. To reduce the effect of this suspended zeolite a titrimetric

15

method for calculating the copper ion concentration could have been used for example using EDTA solution as the titrant and Fast Sulphon F as the indicator.[33] This would also allow a better comparison between the copper and zinc ion exchange processes since the similar methods could compensate for common systematic errors.

6.3   Zinc Exchanged ZSM-5

From section 5.3.2 the percentage of zinc calculated to have been exchanged with the ZSM-5 zeolite was $66 \pm 3\%$. Tamiyakul et al. completed an ion exchange between HZSM-5 with an SiO_2/AlO_3 ratio of 30 and $Zn(NO_3)_2$ at $70\,°C$ for 12 hours and obtained an ion exchange level of $\frac{0.64}{1.5} \times 100\% = 43\%$.[34] The exchange level calculated in this project is expected to be slightly greater than that reported by Tamiyakul et al. due to the lower SiO_2/AlO_3 ratio of ZSM-5 used, however the $66\% - 43\% = 23\%$ difference in ion exchange levels is fairly large and at least art of the difference is likely to be due to the systematic errors discussed (see below): all of which result in an ion exchange value which is too great.

The zeolite suspended in the zinc solution resulted in the aliquot volume being too small since the suspended zeolite displaced some of the solution when the aliquot volume was being measured. This thus reduced the titre volume recorded which can be seen to have inflated the ion exchange level calculated (by inspection of equation 5.3.8.

This may partially explain the anomalous final titre volume obtained in the titration (see run 4 in table 6) since some of the solid zeolite may have settled in the bottom of the volumetric flask, hence for this final titration the pipette contained a greater number of suspended zeolite particles thus reducing the analyte volume and resulting in the anomalously small titre volume.

6.4   Uncertainties

The percentage uncertainty in both of the obtained results is fairly high at 3%, although the actual error is greater than this due to the systematic errors discussed. This could be reduced by instead using Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFT-IR)[35] on the ZSM-5 samples and obtaining the ion exchange level through comparing the integration of the $3570–3630\,cm^{-1}$ peak between the ion exchanged ZSM-5 samples and the original HZSM-5 sample[36] instead of using a titrimetric method on the solutions used, thus reducing the number quantities involved in the calculations and hence reducing the number of errors introduced.

References

(1) Hard and Soft Water, *Zeolite process for water softening*, 2014, `http://hardsoftwater.com/zeolite-process-for-water-softening/` (visited on 11/03/2018).

(2) I. Petrov and T. Michalev, *Proceedings of the University of Ruse*, 2012, **51**, 30–35.

(3) S. Zhang, Q. Yang, Z. Li, W. Gao, C. Wang and Z. Wang, *Analytical Methods*, 2015, **7**, 8165–8171.

(4) D. H. Olson, G. T. Kokotallo, S. L. Lawton and W. M. Meler, *Journal of Physical Chemistry*, 1981, **85**, 2238–2243.

(5) M. Rasouli, N. Yaghobi, S. Chitazan and M. H. Sayyar, *Microporous and Mesoporous Materials*, 2012, **150**, 47–54.

(6) J. Sárkány, *Applied Catalysis A: General*, 1999, **188**, 369–379.

(7) W. M. Meier and D. H. Olson, *Zeolites*, 1992, **12**, 449–656.

(8) W. Locke, *Zeolite Structure*, 1999, `http://www.ch.ic.ac.uk/vchemlib/course/zeolite/structure.html` (visited on 02/03/2018).

(9) A. Han and Y. Qiao, *Journal of Materials Research*, 2009, **24**, 2416–2419.

(10) P. J. Danaher, C. Medino, H. Shevchuk and E. M. Zhang, MA thesis, Worcester Polytechnic Institute, 2017.

(11) P. Gómez-Álvarez, J. Perez-Carbajo, S. R. Balestra and S. Calero, *Journal of Physical Chemistry*, 2016, **120**, 23254–23261.

(12) E. L. Wu, S. L. Lawton, D. H. Olson, J. A. C. Rohrman and G. T. Kokotallo, *Journal of Physical Chemistry*, 1979, **83**, 2777–2781.

(13) R. J. Argauer and G. R. Landolt, *Patent*, 3 702 886 (US), 1972.

(14) Z. R. Ismagilov, R. A. Shkrabina, L. K. Tsikoza, S. A. Yashnik, V. A. Sazonov, V. V. Kuznetsov, M. V. Luzgin, A. V. Kalinkin and H. Veringa, *Kinetics and Catalysis*, 2000, **42**, 847–853.

(15) P. K. Chaudhari, P. K. Saini and S. Chand, *Journal of Scientific and Industrial Research*, 2002, **61**, 810–816.

(16) S. Sato, Y. Yu-u, H. Yahiro, N. Mizuno and M. Iwamoto, *Applied Catalysis*, 1991, **70**, L1–L5.

(17) S. A. Yashnik, Z. R. Ismagilov and V. F. Anufrienko, *Catalysis Today*, 2005, **110**, 310–322.

(18) M. Iwamoto and H. Hamada, *Catalysis Today*, 1991, **10**, 57–71.

(19) X. Niu, J. Gao, Q. Miao, M. Dong, G. Wang, W. Fan, Z. Qin and J. Wang, *Microporous and Mesoporous Materials*, 2014, **197**, 252–261.

(20) X. Wang, J. Zhang, H. Xiao, F. Song, Y. Han and Y. Tan, *RSC Advances*, 2016, **6**, 23428–23437.

(21) L. Sun, Y. Wang, H. Chen, C. Sun, F. Meng, F. Gao and X. Wang, *Catalysis Today*, 2018, DOI: `10.1016/j.cattod.2018.01.015`.

(22) N. Y. Chen, *The Journal of Physical Chemistry*, 1976, **80**, 60–64.

(23) D. H. Olson, W. O. Haag and W. S. Borghard, *Microporous and Mesoporous Materials*, 1999, **35–36**, 435–446.

(24) J. Galbán, S. de Marcos, I. Sanz, C. Ubide and J. Zuriarrain, *Analytical Chemistry*, 2007, **79**, 4763–4767.

(25) V. Dondur, V. Rakić, L. Damjanović, R. Hercigonja and A. Auroux, *Journal of Thermal Analysis and Calorimetry*, 2006, **84**, 233–238.

(26) *CRC Handbook of Chemistry and Physics*, ed. W. M. Haynes, CRC Press, Boca Raton, 97th edn., 2016.

(27) R. Taylor, personal communication, 2018.

(28) S. M. T. Almutairi, B. Mezari, P. C. M. M. Magusin, E. A. Pidko and E. J. M. Hensen, *ACS Catalysis*, 2011, **2**, 71–83.

(29) M. Schreier, S. Teren, L. Belcher, J. R. Regalbuto and J. T. Miller, *Nanotechnology*, 2005, **16**, 582–591.

(30) M. Mhamdi, S. Khaddar-Zine and A. Ghorbel, *Applied Catalysis A: General*, 2009, **357**, 42–50.

(31) H. A. Aleksandrov and G. N. Vayssilov, 2010, **152**, 78–87.

(32) J. Penzien, A. Abraham, J. A. van Bokhoven, A. Jentys, T. E. Müller, C. Sievers and J. A. Lercher, *Journal of Physical Chemistry B*, 2004, **108**, 4116–4126.

(33) D. Denby, *Chemistry Review*, 1999, **9**, 8–9.

(34) S. Tamiyakul, W. Ubolcharoen, D. N. Tungasmita and S. Jongpatiwut, *Catalysis Today*, 2015, **256**, 325–335.

(35) K. Pöllänen, A. Häkkinen, M. Huhtanen, S.-P. Reinikainen, M. Karjalainen, J. Rantanen, M. Louhi-Kultanen and L. Nyström, *Analytica Chimica Acta*, 2005, **544**, 108–117.

(36) L. Yu, S. Huang, S. Zhang, Z. Liu, W. Xin, S. Xie and L. Xu, *ACS Catalysis*, 2012, **2**, 1203–1210.

7 Supplementary Information