Effect of the Copper and Zinc Cations on the Ion Exchange Level Obtained for the Aqueous Phase Ion Exchange Process with the ZSM-5 Zeolite

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Abstract

An investigation into how the ion exchange level for ZSM-5 differs when using copper and zinc cations in an aqueous phase ion exchange process was attempted. The spectrophotometric method utilised for the measurement of the exchange level for the copper cations was found to be ineffective at producing meaningful results within the timescale of the investigation, hence precluding the comparison of the exchange levels for the different metal cations.

1 Aim

This project aimed to compare how the ion exchange level for a HZSM-5 zeolite differs for the aqueous phase ion exchange process with copper and zinc cations.

2 Introduction

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

2.1 Structure

Zeolites are 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

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themselves known as the primary building units and are henceforth generically referred to as XO_4 tetrahedra).[2,7–10] Each aluminium tetrahedron in the SBU introduces a negative charge – since aluminium has a 3+ oxidation state whereas silicon has a 4+ oxidation state – 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 XO_4 tetrahedra which form a pair of five-one units[4,7,12] as shown in figure 1 where the vertices represent the X atoms and the X-O-X bridges are shown as straight lines for clarity which is a reasonable approximation since the X-O-X bond angle is around 140–$150° \approx 180°$ for silicas and aluminosilicates.[7]
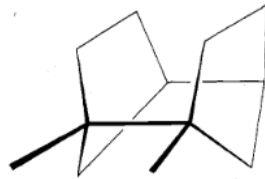

Figure 1: Secondary building unit for ZSM-5 zeolite.[4]

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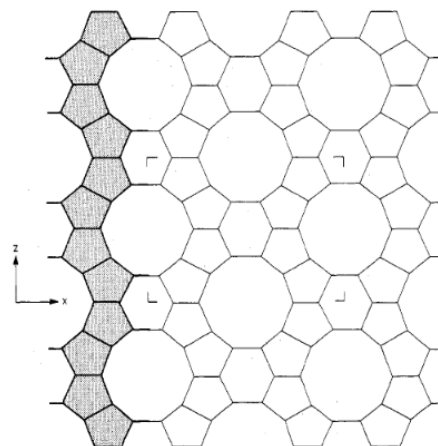

Figure 2: Chain building unit for ZSM-5 zeolite.[4]

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

As there are eight SBUs of twelve tetrahedra per unit cell in ZSM-5 there are $8 \times 12 = 96$ X atoms per cell hence there are $2 \times 96 = 192$ oxygen atoms per cell[7] since there are two oxygen atoms per individual X atom.[13] This gives the unit cell formula given in 2.1.1 where M is a cation with a charge of q, so $\frac{1}{q}$ of these cations are required per negative charge and hence aluminium atom.[14]

$$M_{\frac{n}{q}} Al_n Si_{96-n} O_{192} \cdot x\, H_2O \qquad (2.1.1)$$

2.2 Ion Exchange

These M^{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 low SiO_2/AlO_3 ratio of 23 was used in this investigation since this maximised the number of sites which were available for ion exchange due to the higher aluminium content. In addition zeolites with a high SiO_2/AlO_3 ratio are hydrophobic[9,22,23] hence in aqueous phase ion exchange 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 maximisation of the ion exchange is important since it should accentuate any differences between the ion exchange level with the different cations and make them easier to detect.

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 concentrations of $2.008 \times 10^{-3}\,mol\,dm^{-3}$ 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 solutions was added to $0.4810\,g$ (for the copper

solution) and $0.5274\,\text{g}$ (for the zinc solution) of HZSM-5 zeolite with an $\text{SiO}_2/\text{AlO}_3$ ratio of 23 (forming an opaque white suspension) prior to heating both solutions with stirring at $70\,^\circ\text{C}$ 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 then stored in a fridge for one week until the following laboratory session.

After one week the zeolite had sedimented so clear solution was collected and the remainder was centrifuged for 30 minutes before the supernatant was reintroduced to rest of the solution producing a slightly cloudy copper and a moderately cloudy zinc solution. The solutions were made up to $100.00\,\text{cm}^3$ before the absorbance of the copper solution at $806\,\text{nm}$ was determined (0.110) and $20.00\,\text{cm}^3$ aliquots of the zinc solution in a pH 10 buffer solution $(2\,\text{cm}^3)$ were titrated against a standard ethylenediaminetetraacetate (EDTA) solution (batch A: $0.4993\,\text{mol}\,\text{dm}^{-3}$) with an eriochrome black T 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
$\text{CuSO}_4 \cdot 5\,\text{H}_2\text{O}$	0.5014
HZSM-5	0.4810

Table 2: Spectrophotometric results for the copper sulphate solutions.

Substance	Absorbance
Standard Solution	0.484
Post-Reaction Solution	0.110

The uncertainty in these absorbance values 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.

Values of $k_2 = 4.5 \times 10^{-4}$ and $k_3 = 27 \times 10^{-4}$ were used (recorded by Galbán et al. for the PerkinElmer Lambda 5 spectrophotometer with ferroin solution)[24] since they

produce the largest overall uncertainty of values recorded by Galbán et al., hence giving the most generous estimate in the uncertainty of the absorbances recorded. 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 thus gives:

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

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

4.2 Zinc-Exchanged Zeolite

Table 3: Mass 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:

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

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 run (see table 5):

Table 5: Titration results from standardisation of the batch A EDTA solution with the 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. There are two Al atoms in Al_2O_3 compared to one Si atom in SiO_2, hence $Si/Al = \frac{23}{2} = 11.5$.

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

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

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 thus gives:

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

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} respectively be the actual amount, mass and Mr of the cation exchanged.

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

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.

$$n_{\text{CuSO}_4} = \frac{m_{\text{CuSO}_4 \cdot 5\,\text{H}_2\text{O}}}{Mr_{\text{CuSO}_4 \cdot 5\,\text{H}_2\text{O}}}$$
$$[\text{CuSO}_4]_{\text{std.}} = \frac{n_{\text{CuSO}_4}}{V_{\text{Cu}_{\text{std.}}}}$$
$$= \frac{m_{\text{CuSO}_4 \cdot 5\,\text{H}_2\text{O}}}{V_{\text{Cu}_{\text{std.}}} Mr_{\text{CuSO}_4 \cdot 5\,\text{H}_2\text{O}}} \tag{5.2.1}$$

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:

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

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

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

Substituting equation 5.2.4 into 5.2.6:

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

The amount of Cu^{2+} exchanged ($n_{Cu_{ex.}}$) can hence be determined using equations 5.2.1 and 5.2.7 where $V_{Cu_{react.}}$ is the volume of the standard copper solution added to the HZSM-5.

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$$n_{\mathrm{Cu_{ex.}}} = [\mathrm{CuSO_4}]V_{\mathrm{Cu_{react.}}} - n_{\mathrm{Cu_{prod.}}}$$

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

$$= \frac{m_{\mathrm{CuSO_4 \cdot 5\,H_2O}}\left(A_{\mathrm{Cu_{std.}}}V_{\mathrm{Cu_{react.}}} - A_{\mathrm{Cu_{prod.}}}V_{\mathrm{Cu_{prod.}}}\right)}{A_{\mathrm{Cu_{std.}}}V_{\mathrm{Cu_{std.}}}Mr_{\mathrm{CuSO_4 \cdot 5\,H_2O}}} \qquad (5.2.8)$$

Substituting equation 5.2.8 into equation 5.1.2 as n_{cation} and setting $q = 2$ hence gives:

$$\% \ \mathrm{Cu^{2+}} \ \mathrm{Exchanged} = \frac{2Mr_{\mathrm{HZSM\text{-}5\ unit\ cell}}m_{\mathrm{CuSO_4 \cdot 5\,H_2O}}\left(A_{\mathrm{Cu_{std.}}}V_{\mathrm{Cu_{react.}}} - A_{\mathrm{Cu_{prod.}}}V_{\mathrm{Cu_{prod.}}}\right)}{7.68m_{\mathrm{HZSM\text{-}5}}A_{\mathrm{Cu_{std.}}}V_{\mathrm{Cu_{std.}}}Mr_{\mathrm{CuSO_4 \cdot 5\,H_2O}}}$$
$$\times \ 100\,\%$$
$$(5.2.9)$$

Using 5.2.9 with:

$$Mr_{\mathrm{HZSM\text{-}5\ unit\ cell}} = 6217.613\,\mathrm{g\,mol^{-1}}\ \text{from equation 5.1.1}$$
$$m_{\mathrm{CuSO_4 \cdot 5\,H_2O}} = 0.501\,40 \pm 0.000\,05\,\mathrm{g}\ \text{from table 1}$$
$$A_{\mathrm{Cu_{std.}}} = 0.484 \pm 0.001\ \text{from table 2 and equation 4.1.2}$$
$$V_{\mathrm{Cu_{react.}}} = 20.00 \pm 0.06 \times 10^{-3}\,\mathrm{dm^3}\ \text{from method (section 3)}$$
$$A_{\mathrm{Cu_{prod.}}} = 0.110 \pm 0.001\ \text{from table 2 and equation 4.1.3}$$
$$V_{\mathrm{Cu_{prod.}}} = 100.00 \pm 0.20 \times 10^{-3}\,\mathrm{dm^3}\ \text{from method (section 3)}$$
$$m_{\mathrm{HZSM\text{-}5}} = 0.481\,00 \pm 0.000\,05\,\mathrm{g}\ \text{from table 1}$$
$$V_{\mathrm{Cu_{std.}}} = 50.00 \pm 0.06 \times 10^{-3}\,\mathrm{dm^3}\ \text{from method (section 3)}$$
$$Mr_{\mathrm{CuSO_4 \cdot 5\,H_2O}} = 249.685\,\mathrm{g\,mol^{-1}}{}^{26}$$

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

5.2.3 Error Propagation

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

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

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

$$(5.2.10)$$

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

$$\delta S = \left((\delta(A_{Cu_{\text{std.}}}V_{Cu_{\text{react.}}}))^2 + (\delta(A_{Cu_{\text{prod.}}}V_{Cu_{\text{prod.}}}))^2\right)^{1/2}$$

$$= \left(\left(A_{Cu_{\text{std.}}}V_{Cu_{\text{react.}}}\left(\left(\frac{\delta A_{Cu_{\text{std.}}}}{A_{Cu_{\text{std.}}}}\right)^2 + \left(\frac{\delta V_{Cu_{\text{react.}}}}{V_{Cu_{\text{react.}}}}\right)^2\right)^{1/2}\right)^2\right.$$

$$\left. + \left(A_{Cu_{\text{prod.}}}V_{Cu_{\text{prod.}}}\left(\left(\frac{\delta A_{Cu_{\text{prod.}}}}{A_{Cu_{\text{prod.}}}}\right)^2 + \left(\frac{\delta V_{Cu_{\text{prod.}}}}{V_{Cu_{\text{prod.}}}}\right)^2\right)^{1/2}\right)^2\right)^{1/2}$$

$$= \left(A_{Cu_{\text{std.}}}^2 V_{Cu_{\text{react.}}}^2\left(\left(\frac{\delta A_{Cu_{\text{std.}}}}{A_{Cu_{\text{std.}}}}\right)^2 + \left(\frac{\delta V_{Cu_{\text{react.}}}}{V_{Cu_{\text{react.}}}}\right)^2\right)\right.$$

$$\left. + A_{Cu_{\text{prod.}}}^2 V_{Cu_{\text{prod.}}}^2\left(\left(\frac{\delta A_{Cu_{\text{prod.}}}}{A_{Cu_{\text{prod.}}}}\right)^2 + \left(\frac{\delta V_{Cu_{\text{prod.}}}}{V_{Cu_{\text{prod.}}}}\right)^2\right)\right)^{1/2}$$

$$(5.2.11)$$

Hence substituting equation 5.2.11 into 5.2.10 gives:

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

$$+ \frac{A_{\text{Cu}_{\text{std.}}}^2 V_{\text{Cu}_{\text{react.}}}^2 \left(\left(\frac{\delta A_{\text{Cu}_{\text{std.}}}}{A_{\text{Cu}_{\text{std.}}}} \right)^2 + \left(\frac{\delta V_{\text{Cu}_{\text{react.}}}}{V_{\text{Cu}_{\text{react.}}}} \right)^2 \right) + A_{\text{Cu}_{\text{prod.}}}^2 V_{\text{Cu}_{\text{prod.}}}^2 \left(\left(\frac{\delta A_{\text{Cu}_{\text{prod.}}}}{A_{\text{Cu}_{\text{prod.}}}} \right)^2 + \left(\frac{\delta V_{\text{Cu}_{\text{prod.}}}}{V_{\text{Cu}_{\text{prod.}}}} \right)^2 \right)}{\left(A_{\text{Cu}_{\text{std.}}} V_{\text{Cu}_{\text{react.}}} - A_{\text{Cu}_{\text{prod.}}} V_{\text{Cu}_{\text{prod.}}} \right)^2}$$

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

$$(5.2.12)$$

Substituting values into equation 5.2.12 yields:

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

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

5.3 Calculations for Zinc Solution

5.3.1 Determination of EDTA Solution (Batch A) Concentration

Let: $V_{\text{Zn}_{\text{std.}}}$ be the volume, $[\text{ZnSO}_4]_{\text{std.}}$ be the concentration and $m_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}_{\text{std.}}}$ be the mass of $\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}$ used for the preparation of the ZnSO_4 standard solution used to standardise the EDTA solution. Thus:

$$[\text{ZnSO}_4]_{\text{std.}} = \frac{m_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}_{\text{std.}}}}{Mr_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}} V_{\text{Zn}_{\text{std.}}}} \qquad (5.3.1)$$

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

$$[\text{EDTA}^{4-}] = \frac{n_{\text{Zn}_{\text{std. analyte}}}}{V_{\text{EDTA}_{\text{std.}}}} = \frac{[\text{ZnSO}_4]_{\text{std.}} V_{\text{Zn}_{\text{std. aliquot}}}}{V_{\text{EDTA}_{\text{std.}}}} \qquad (5.3.2)$$

Substituting equation 5.3.1 into equation 5.3.2 gives:

$$[\text{EDTA}^{4-}] = \frac{m_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}_{\text{std.}}} V_{\text{Zn}_{\text{std. aliquot}}}}{Mr_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}} V_{\text{Zn}_{\text{std.}}} V_{\text{EDTA}_{\text{std.}}}} \tag{5.3.3}$$

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

For the standard ZnSO_4 solution added to the HZSM-5 let $m_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}_{\text{orig.}}}$ be the mass of $\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}$ used and let $V_{\text{Zn}_{\text{std. orig.}}}$ and $[\text{ZnSO}_4]_{\text{std. orig.}}$ be the volume and concentration of the solution respectively.

$$[\text{ZnSO}_4]_{\text{std. orig.}} = \frac{m_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}_{\text{orig.}}}}{Mr_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}} V_{\text{Zn}_{\text{std. orig.}}}} \tag{5.3.4}$$

Using equation 5.3.4 with $V_{\text{Zn}_{\text{orig.}}}$ as the volume of the standard solution used in the ion-exchange process:

$$\begin{aligned}
n_{\text{Zn}_{\text{orig.}}} &= [\text{ZnSO}_4]_{\text{std. orig.}} V_{\text{Zn}_{\text{orig.}}} \\
&= \frac{m_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}_{\text{orig.}}} V_{\text{Zn}_{\text{orig.}}}}{Mr_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}} V_{\text{Zn}_{\text{std. orig.}}}}
\end{aligned} \tag{5.3.5}$$

The amount of zinc remaining in solution after the ion exchange $(n_{\text{Zn}_{\text{prod.}}})$ can be calculated using equation 5.3.3 with $V_{\text{Zn}_{\text{prod.}}}$ being the volume the solution after the reaction and $V_{\text{Zn}_{\text{prod. aliquot}}}$ being the volume of the aliquot titrated. By equation 4.2.1 the stoichiometric ratio for the reaction between the Zn^{2+} and EDTA^{4-} in the titration is 1:1, so:

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

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

$$n_{\text{Zn}_{\text{ex.}}} = n_{\text{Zn}_{\text{orig.}}} - n_{\text{Zn}_{\text{prod.}}}$$

$$= \frac{m_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}_{\text{orig.}}} V_{\text{Zn}_{\text{orig.}}}}{Mr_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}} V_{\text{Zn}_{\text{std. orig.}}}} - \frac{V_{\text{EDTA}_{\text{prod.}}} m_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}_{\text{std.}}} V_{\text{Zn}_{\text{std. aliquot}}} V_{\text{Zn}_{\text{prod.}}}}{V_{\text{Zn}_{\text{prod. aliquot}}} Mr_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}} V_{\text{Zn}_{\text{std.}}} V_{\text{EDTA}_{\text{std.}}}}$$

$$= \frac{V_{\text{Zn}_{\text{prod. aliquot}}} V_{\text{Zn}_{\text{std.}}} V_{\text{EDTA}_{\text{std.}}} m_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}_{\text{orig.}}} V_{\text{Zn}_{\text{orig.}}}}{V_{\text{Zn}_{\text{std. orig.}}} V_{\text{Zn}_{\text{prod. aliquot}}} Mr_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}} V_{\text{Zn}_{\text{std.}}} V_{\text{EDTA}_{\text{std.}}}}$$

$$- \frac{V_{\text{Zn}_{\text{std. orig.}}} V_{\text{EDTA}_{\text{prod.}}} m_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}_{\text{std.}}} V_{\text{Zn}_{\text{std. aliquot}}} V_{\text{Zn}_{\text{prod.}}}}{V_{\text{Zn}_{\text{std. orig.}}} V_{\text{Zn}_{\text{prod. aliquot}}} Mr_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}} V_{\text{Zn}_{\text{std.}}} V_{\text{EDTA}_{\text{std.}}}}$$

(5.3.7)

Hence substituting equation 5.3.7 into 5.1.2 for n_{cation} and setting $q = 2$ gives:

$$\% \text{ Zn Exchanged} = \frac{2 Mr_{\text{HZSM-5 unit cell}}}{7.68 m_{\text{HZSM-5}} V_{\text{Zn}_{\text{std. orig.}}} V_{\text{Zn}_{\text{prod. aliquot}}} Mr_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}} V_{\text{Zn}_{\text{std.}}} V_{\text{EDTA}_{\text{std.}}}}$$

$$\times (V_{\text{Zn}_{\text{prod. aliquot}}} V_{\text{Zn}_{\text{std.}}} V_{\text{EDTA}_{\text{std.}}} m_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}_{\text{orig.}}} V_{\text{Zn}_{\text{orig.}}}$$

$$- V_{\text{Zn}_{\text{std. orig.}}} V_{\text{EDTA}_{\text{prod.}}} m_{\text{ZnSO}_4 \cdot 7\,\text{H}_2\text{O}_{\text{std.}}} V_{\text{Zn}_{\text{std. aliquot}}} V_{\text{Zn}_{\text{prod.}}}) \times 100\,\%$$

(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:

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

$$(5.3.9)$$

Using the same process demonstrated in section 5.2.3 used for equation 5.2.11 to expand the subtraction within equation 5.3.9 hence gives equation 5.3.10 below:

$$\delta v_{\mathrm{Zn}} = v_{\mathrm{Zn}} \left(\left(\frac{\delta Mr_{\mathrm{HZSM\text{-}5\ unit\ cell}}}{Mr_{\mathrm{HZSM\text{-}5\ unit\ cell}}} \right)^2 + \left(\frac{\delta m_{\mathrm{HZSM\text{-}5}}}{m_{\mathrm{HZSM\text{-}5}}} \right)^2 + \left(\frac{\delta V_{\mathrm{Zn_{std.\ orig.}}}}{V_{\mathrm{Zn_{std.\ orig.}}}} \right)^2 + \left(\frac{\delta V_{\mathrm{Zn_{prod.\ aliquot}}}}{V_{\mathrm{Zn_{prod.\ aliquot}}}} \right)^2 \right.$$

$$+ \left(\frac{\delta Mr_{\mathrm{ZnSO_4 \cdot 7\,H_2O}}}{Mr_{\mathrm{ZnSO_4 \cdot 7\,H_2O}}} \right)^2 + \left(\frac{\delta V_{\mathrm{Zn_{std.}}}}{V_{\mathrm{Zn_{std.}}}} \right)^2 + \left(\frac{\delta V_{\mathrm{EDTA_{std.}}}}{V_{\mathrm{EDTA_{std.}}}} \right)^2$$

$$+ \frac{V_{\mathrm{Zn_{prod.\ aliquot}}}^2 V_{\mathrm{Zn_{std.}}}^2 V_{\mathrm{EDTA_{std.}}}^2 m_{\mathrm{ZnSO_4 \cdot 7\,H_2O_{orig.}}}^2 V_{\mathrm{Zn_{orig.}}}^2 \left(\left(\frac{\delta V_{\mathrm{Zn_{prod.\ aliquot}}}}{V_{\mathrm{Zn_{prod.\ aliquot}}}} \right)^2 \right.}{\left(V_{\mathrm{Zn_{prod.\ aliquot}}} V_{\mathrm{Zn_{std.}}} V_{\mathrm{EDTA_{std.}}} m_{\mathrm{ZnSO_4 \cdot 7\,H_2O_{orig.}}} V_{\mathrm{Zn_{orig.}}} - V_{\mathrm{Zn_{std.\ orig.}}} V_{\mathrm{EDTA_{prod.}}} \right.}$$

$$\frac{\left. + \left(\frac{\delta V_{\mathrm{Zn_{std.}}}}{V_{\mathrm{Zn_{std.}}}} \right)^2 + \left(\frac{\delta V_{\mathrm{EDTA_{std.}}}}{V_{\mathrm{EDTA_{std.}}}} \right)^2 + \left(\frac{\delta m_{\mathrm{ZnSO_4 \cdot 7\,H_2O_{orig.}}}}{m_{\mathrm{ZnSO_4 \cdot 7\,H_2O_{orig.}}}} \right)^2 + \left(\frac{\delta V_{\mathrm{Zn_{orig.}}}}{V_{\mathrm{Zn_{orig.}}}} \right)^2 \right) + V_{\mathrm{Zn_{std.\ orig.}}}^2}{\left. m_{\mathrm{ZnSO_4 \cdot 7\,H_2O_{std.}}} V_{\mathrm{Zn_{std.\ aliquot}}} V_{\mathrm{Zn_{prod.}}} \right)^2}$$

$$\frac{V_{\mathrm{EDTA_{prod.}}}^2 m_{\mathrm{ZnSO_4 \cdot 7\,H_2O_{std.}}}^2 V_{\mathrm{Zn_{std.\ aliquot}}}^2 V_{\mathrm{Zn_{prod.}}}^2 \left(\left(\frac{\delta V_{\mathrm{Zn_{std.\ orig.}}}}{V_{\mathrm{Zn_{std.\ orig.}}}} \right)^2 + \left(\frac{\delta V_{\mathrm{EDTA_{prod.}}}}{V_{\mathrm{EDTA_{prod.}}}} \right)^2 \right.}{}$$

$$\left. \frac{+ \left(\frac{\delta m_{\mathrm{ZnSO_4 \cdot 7\,H_2O_{std.}}}}{m_{\mathrm{ZnSO_4 \cdot 7\,H_2O_{std.}}}} \right)^2 + \left(\frac{\delta V_{\mathrm{Zn_{std.\ aliquot}}}}{V_{\mathrm{Zn_{std.\ aliquot}}}} \right)^2 + \left(\frac{\delta V_{\mathrm{Zn_{prod.}}}}{V_{\mathrm{Zn_{prod.}}}} \right)^2 \right)}{} \right)^{1/2}$$

(5.3.10)

Substituting values into equation 5.3.10 gives:

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

Hence the percentage ion exchange level of Zn^{2+} is $66 \pm 3\,\%$.

6 Discussion

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 still allowing direct comparison of the ion exchange results.

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

Both the copper and zinc solutions were cloudy following the centrifugation indicating that some ZSM-5 remained suspended in the solutions. Further centrifugation would have reduced the amount of suspended zeolite from the solutions and hence the errors resultant from this (see sections 6.2 and 6.3). 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 allowing the possibility of an ion exchange level greater than the maximum calculated,[28,29] however the exchange of the monomeric species is thermodynamically preferred and the alternative 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, thus they can be assumed to have no effect on the ion exchange level obtained.

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 which increased the absorbance value of the sample thus resulting in the negative

yield calculated. To reduce the effect of this suspended zeolite a titrimetric 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 $70\,^\circ C$ for 12 hours and obtained an ion exchange level of $\frac{0.64\%}{1.5\%} \times 100\% = 43\%$.[34] The SiO_2/AlO_3 ratio of the HZSM-5 used by Tamiyakul et al. is larger than that used in this project, hence a higher ion exchange level is expected, however Yashnik et al. only obtained a 22% higher ion exchange level with $CuSO_4$ while using HZSM-5 with an SiO_2/AlO_3 ratio of 17 compared to when HZSM-5 with a ratio of 30 was used.[17] The difference in the SiO_2/AlO_3 ratio of the HZSM-5 between this project and the HZSM-5 used by Tamiyakul et al. is almost half of the difference between the samples compared by Yashnik et al. while the difference in ion exchange level is slightly greater (23%), thus suggesting that the ion exchange level obtained is too high.

This can be explained by the losses in the centrifugation described earlier and also since the post-ion exchange solution contained suspended zeolite hence the aliquot volume in the titration was too small since the suspended zeolite displaced some of the solution when the 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 also 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 further 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 quite 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] This would result in a smaller error compared

to the titrimetric method since the number of measurements required for the calculation is much less hence reducing the number of errors introduced.

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7 Supplementary Information