

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

Sam White

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.<sup>1,2</sup> This project was completed using the ZSM-5 (Zeolite Socony Mobil-5)<sup>3</sup> 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.<sup>4-6</sup>

### 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  $[\text{SiO}_4]$  or  $[\text{AlO}_4]^-$  (which are themselves the primary building units).<sup>2,7-10</sup> 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.<sup>2,9-11</sup> The ZSM-5 zeolite used is a pentasil<sup>4,10</sup> zeolite (constructed of eight five-membered rings) with an SBU containing twelve  $\text{AO}_4$  tetrahedra which form a pair of five-one units<sup>4,7,12</sup> 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  $140\text{--}150^\circ \approx 180^\circ$  for silicas and aluminosilicates and the A atoms are represented by the vertices).<sup>7</sup>

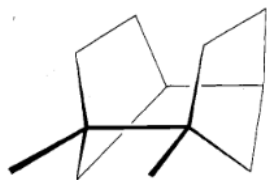


Figure 1: Secondary building unit for ZSM-5 zeolite.<sup>4</sup>

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.<sup>4</sup> 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.<sup>4</sup>

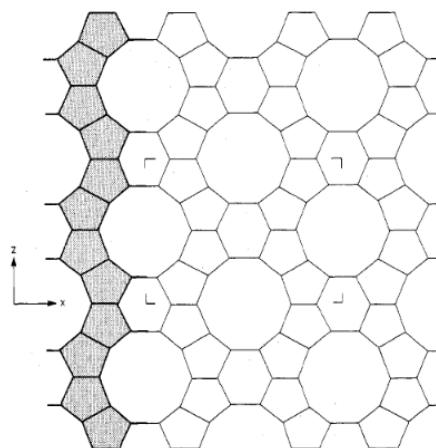


Figure 3: Layer of ZSM-5 zeolite.<sup>4</sup>

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<sup>13</sup> so per unit

cell there are  $2 \times 96 = 192$  oxygen atoms.<sup>7</sup> 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.<sup>14</sup>



## 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.<sup>5,9,15</sup>

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<sub>2</sub>–C<sub>4</sub> hydrocarbons.<sup>14,16,17</sup> 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.<sup>18</sup>

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.<sup>19,20</sup> 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.<sup>21</sup>

A ZSM-5 zeolite with a SiO<sub>2</sub>/AlO<sub>3</sub> 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<sup>9,22,23</sup> hence the cation solution does not spontaneously enter the zeolite nanopores so ion-exchange happens only at sites close to the pore entrance.<sup>9,23</sup> This will thus reduce the percentage uncertainties in the values recorded.

## 3 Experimental

Standard solutions of Cu<sup>2+</sup> and Zn<sup>2+</sup> (50.00 cm<sup>3</sup>) were made using CuSO<sub>4</sub> · 5 H<sub>2</sub>O and ZnSO<sub>4</sub> · 7 H<sub>2</sub>O with concentration  $2.008 \times 10^{-3} \text{ mol dm}^{-3}$  and  $2.02 \times 10^{-3} \text{ mol dm}^{-3}$  respectively. The absorbance of the standard copper sulphate solution was taken at 806 nm (0.484) then 20.00 cm<sup>3</sup> 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<sub>3</sub>:SiO<sub>2</sub> 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  $100.00\text{ cm}^3$  before the absorbance of the copper solution at  $806\text{ nm}$  was determined ( $0.110$ ) and the zinc solution was titrated against a standard EDTA solution ( $0.4993\text{ mol dm}^{-3}$ ) with  $2\text{ cm}^3$  of a pH 10 buffer solution and eriochrome black T as the indicator.

## 4 Results

### 4.1 Copper-Exchanged Zeolite

Table 1: Masses used in CuZSM-5 preparation.

Substance	Mass / g
$\text{CuSO}_4 \cdot 5\text{ H}_2\text{O}$	0.5014
HZSM-5	0.4810

Table 2: Spectrophotometric results.

Substance	Absorbance
Standard Solution	0.484
Post-Reaction Solution	0.110

### 4.2 Zinc-Exchanged Zeolite

Table 3: Masses used in ZnZSM-5 preparation.

Substance	Mass / g
$\text{ZnSO}_4 \cdot 7\text{ H}_2\text{O}$	0.6331
HZSM-5	0.5274

Table 4: Titration results from standardisation of EDTA solution with standard zinc sulphate solution.

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

Table 5: Titration results between zinc solution after ion-exchange process and standardised EDTA solution.

Run	Start Volume / cm <sup>3</sup>	End Volume / cm <sup>3</sup>	Titre Volume / cm <sup>3</sup>
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

## 5 Calculations

### 5.1 Calculation of Maximum Theoretical Number of Ion Exchanges

The SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> 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:

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

$$= \frac{7.68}{q} Mr_{\text{cation}} + 5759.4692 \text{g mol}^{-1} + x(450.375 \text{g mol}^{-1})$$

Thus for HZSM-5 where the cation is  $H^+$  and  $x \approx 25$ .<sup>24</sup>

$$\begin{aligned} Mr_{\text{HZSM-5 unit cell}} &= \frac{7.68}{1} \times 1.008 \text{ g mol}^{-1} + (5759.49692 + 25(450.375)) \text{ g mol}^{-1} \\ &= 6217.6134 \text{ g mol}^{-1} \end{aligned} \quad (5.1.1)$$

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

$$\begin{aligned} n_{\text{HZSM-5 unit cell}} &= \frac{m_{\text{HZSM-5}}}{Mr_{\text{HZSM-5 unit cell}}} \\ n_{\text{max. cation}} &= \frac{7.68}{q} n_{\text{HZSM-5 unit cell}} \\ &= \frac{7.68}{q} \frac{m_{\text{HZSM-5}}}{Mr_{\text{HZSM-5 unit cell}}} \\ \% \text{ Exchanged} &= \frac{n_{\text{cation}}}{n_{\text{max. cation}}} \times 100 \% \\ &= \frac{q Mr_{\text{HZSM-5 unit cell}} n_{\text{cation}}}{7.68 m_{\text{HZSM-5}}} \times 100 \% \end{aligned} \quad (5.1.2)$$

## 5.2 Calculations for Copper Solution

### 5.2.1 Determination of Molar Extinction Coefficient

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

$$\begin{aligned} n_{\text{CuSO}_4} &= \frac{m_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}}{Mr_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}} \\ [\text{CuSO}_4]_{\text{std.}} &= \frac{n_{\text{CuSO}_4}}{V_{\text{Cu std.}}} \\ &= \frac{m_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}}{V_{\text{Cu std.}} Mr_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}} \end{aligned} \quad (5.2.1)$$

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

$$A = \epsilon cl \quad (5.2.2)$$

$$\epsilon = \frac{A}{cl} \quad (5.2.3)$$

Hence using equations 5.2.1 and 5.2.3 with  $A_{\text{Cu}_{\text{std.}}}$  being the absorbance of the standard  $\text{CuSO}_4$  solution:

$$\begin{aligned}\epsilon_{\text{CuSO}_4} &= \frac{A_{\text{Cu}_{\text{std.}}}}{[\text{CuSO}_4]_{\text{std.}} l} \\ &= \frac{A_{\text{Cu}_{\text{std.}}} V_{\text{Cu}_{\text{std.}}} M_{r\text{CuSO}_4 \cdot 5\text{H}_2\text{O}}{l m_{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}}}\end{aligned}\quad (5.2.4)$$

This hence gives:

$$\begin{aligned}\epsilon_{\text{CuSO}_4} &= \frac{0.484 \times 50.00 \times 10^{-3} \text{ dm}^3 \times (63.546 + 32.066 + 4(15.999) + 5(2(1.008) + 15.999)) \text{ g mol}^{-1}}{1.0 \text{ cm} \times 0.5014 \text{ g}} \\ &= \frac{0.484 \times 50.00 \times 10^{-3} \text{ dm}^3 \times 249.677 \text{ g mol}^{-1}}{1.0 \text{ cm} \times 0.5014 \text{ g}} = 12.05 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}\end{aligned}\quad (5.2.5)$$

### 5.2.2 Determination of Percentage of $\text{Cu}^{2+}$ Exchanged Compared to the Theoretical Maximum

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

$$c = \frac{A}{\epsilon l}\quad (5.2.6)$$

Letting  $[\text{CuSO}_4]_{\text{prod.}}$  be the concentration,  $A_{\text{Cu}_{\text{prod.}}}$  be the absorbance,  $n_{\text{Cu}_{\text{prod.}}}$  be the amount of  $\text{Cu}^{2+}$  ions and  $V_{\text{Cu}_{\text{prod.}}}$  be the volume of the solution after the ion-exchange reaction while using equation 5.2.6:

$$\begin{aligned}[\text{CuSO}_4]_{\text{prod.}} &= \frac{A_{\text{Cu}_{\text{prod.}}}}{\epsilon_{\text{CuSO}_4} l} \\ n_{\text{Cu}_{\text{prod.}}} &= [\text{CuSO}_4]_{\text{prod.}} V_{\text{Cu}_{\text{prod.}}} \\ &= \frac{A_{\text{Cu}_{\text{prod.}}} V_{\text{Cu}_{\text{prod.}}}}{\epsilon_{\text{CuSO}_4} l}\end{aligned}\quad (5.2.7)$$

Substituting equation 5.2.4 into 5.2.7:

$$n_{\text{Cu}_{\text{prod.}}} = \frac{A_{\text{Cu}_{\text{prod.}}} V_{\text{Cu}_{\text{prod.}}} m_{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}}{A_{\text{Cu}_{\text{std.}}} V_{\text{Cu}_{\text{std.}}} M_{r\text{CuSO}_4 \cdot 5\text{H}_2\text{O}}\quad (5.2.8)$$

Using equations 5.2.1 and 5.2.8 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.

$$\begin{aligned}
n_{\text{Cuex.}} &= [\text{CuSO}_4]V_{\text{Cureact.}} - n_{\text{Cuprod.}} \\
&= \frac{m_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}V_{\text{Cureact.}}}{V_{\text{Custd.}}Mr_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}} - \frac{A_{\text{Cuprod.}}V_{\text{Cuprod.}}m_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}}{A_{\text{Custd.}}V_{\text{Custd.}}Mr_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}} \\
&= \frac{m_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}(A_{\text{Custd.}}V_{\text{Cureact.}} - A_{\text{Cuprod.}}V_{\text{Cuprod.}})}{A_{\text{Custd.}}V_{\text{Custd.}}Mr_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}} \quad (5.2.9)
\end{aligned}$$

Substituting equation 5.2.9 into equation 5.1.2 and setting  $q = 2$  hence gives:

$$\% \text{ Cu}^{2+} \text{ Exchanged} = \frac{2Mr_{\text{HZSM-5 unit cell}}m_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}(A_{\text{Custd.}}V_{\text{Cureact.}} - A_{\text{Cuprod.}}V_{\text{Cuprod.}})}{7.68m_{\text{HZSM-5}}A_{\text{Custd.}}V_{\text{Custd.}}Mr_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}} \times 100 \% \quad (5.2.10)$$

Using 5.2.10 with:

$$\begin{aligned}
Mr_{\text{HZSM-5 unit cell}} &= 6217.6134 \text{ g mol}^{-1} \text{ from equation 5.1.1} \\
m_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}} &= 0.50140 \pm 0.00005 \text{ g from table 4.1} \\
A_{\text{Custd.}} &= 0.484 \text{ from table 4.1} \\
V_{\text{Cureact.}} &= 20.00 \pm 0.06 \times 10^{-3} \text{ dm}^3 \\
A_{\text{Cuprod.}} &= 0.110 \text{ from table 4.1} \\
V_{\text{Cuprod.}} &= 100.00 \pm 0.20 \times 10^{-3} \text{ dm}^3 \\
m_{\text{HZSM-5}} &= 0.48100 \pm 0.00005 \text{ g from table 4.1} \\
V_{\text{Custd.}} &= 50.00 \pm 0.06 \times 10^{-3} \text{ dm}^3 \\
Mr_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}} &= 249.577 \text{ g mol}^{-1} \text{ from equation 5.2.5}
\end{aligned}$$

$$\begin{aligned}
\% \text{ Cu}^{2+} \text{ Exchanged} &= \frac{2 \times 6217.6134 \text{ g mol}^{-1} \times 0.50140 \text{ g} (0.484 \times 20.00 - 0.110 \times 100.00) 10^{-3} \text{ dm}^3}{7.68 \times 0.4810 \text{ g} \times 0.484 \times 50.00 \times 10^{-3} \text{ dm}^3 \times 249.577 \text{ g mol}^{-1}} \\
&\times 100 \% \\
&= -18 \%
\end{aligned}$$

### 5.2.3 Error Propagation

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



$$\begin{aligned}
\delta v_{\text{Cu}} = v_{\text{Cu}} & \left( \left( \frac{\delta Mr_{\text{HZSM-5 unit cell}}}{Mr_{\text{HZSM-5 unit cell}}} \right)^2 + \left( \frac{\delta m_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}}{m_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}} \right)^2 \right. \\
& + \frac{A_{\text{Cu}_{\text{std.}}}^2 V_{\text{Cu}_{\text{react.}}}^2 \left( \left( \frac{\delta A_{\text{Cu}_{\text{std.}}}}{A_{\text{Cu}_{\text{std.}}}} \right)^2 + \left( \frac{\delta V_{\text{Cu}_{\text{react.}}}}{V_{\text{Cu}_{\text{react.}}}} \right)^2 \right) + A_{\text{Cu}_{\text{prod.}}}^2 V_{\text{Cu}_{\text{react.}}}^2 \left( \left( \frac{\delta A_{\text{Cu}_{\text{prod.}}}}{A_{\text{Cu}_{\text{prod.}}}} \right)^2 + \left( \frac{\delta V_{\text{Cu}_{\text{prod.}}}}{V_{\text{Cu}_{\text{prod.}}}} \right)^2 \right)}{(A_{\text{Cu}_{\text{std.}}} V_{\text{Cu}_{\text{react.}}} - A_{\text{Cu}_{\text{prod.}}} V_{\text{Cu}_{\text{prod.}}})^2} \\
& \left. + \left( \frac{\delta m_{\text{HZSM-5}}}{m_{\text{HZSM-5}}} \right)^2 + \left( \frac{\delta A_{\text{Cu}_{\text{std.}}}}{A_{\text{Cu}_{\text{std.}}}} \right)^2 + \left( \frac{\delta V_{\text{Cu}_{\text{std.}}}}{V_{\text{Cu}_{\text{std.}}}} \right)^2 + \left( \frac{\delta Mr_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}}{Mr_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}} \right)^2 \right)^{1/2}
\end{aligned} \tag{5.2.11}$$

Substituting values into equation 5.2.11 thus yields:

$$\delta v_{\text{Cu}} = \pm 0.00 \%$$

So the percentage of  $\text{Cu}^{2+}$  exchanged is  $-18 \pm \%$ .

### 5.3 Calculation of Ion-Exchange Efficiency for Zinc Solution

## 6 Analysis

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

## 7 Supplementary Information