CHAPTER 3

Experimental Procedures

3.1 Raw Materials

Zeolite Na-Y powder (trade name CBV-100) which contains sodium as the nominal cation, from Zeolyst International, (Delfzijl, The Netherlands), was used after being dried in the oven at 40°C overnight. The elemental composition of the zeolite is listed in Appendix 1, as characterized through XRF. All other reagents were used as received without further purification. Ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$) [Assay 99%] from Sigma Chemicals (St. Louis, Missouri, USA) was used. Sodium hydroxide (NaOH) [Assay 97.0%] mini pearls were purchased from Univar (Seven Hills, NSW, Australia). Hydrogen peroxide (H_2O_2) 30% was obtained from J.T. Baker (Philipsburg, NJ, USA). Deionized water was used throughout the experiment.

3.2 Apparatus

Deionized water was obtained from an ultra pure water system Elga UHQ (Ultra High Quality). The water was used when its resistivity reached 16-18 MΩ/cm. A microbalance (Sartorius Electronic Precision Balance) was used for sample weighing. Stirring and heating were done on a PMC hot plate magnetic stirrer with Teflon-coated magnetic stirring bars. Ion exchange of the zeolite Na-Y powder was performed using Schott Duran filter crucibles (Grade 3, 10-16 μm) with the aid of vacuum suction provided by a high vacuum pump from Edwards High Vacuum Ltd., England. The exchanged zeolite-iron paste was washed with deionized water in an EBA 12 centrifuge from Hettich Zentrifugen. Fast drying of samples were done in a Carbolite oven while dried samples were kept in a Weifo electronic dry cabinet with a constant relative humidity of 38%.

3.3 Preparation of Reacting Solutions

In order to prepare five different samples, the synthesis procedure involved reaction of 100 ml of 0.1 M $FeCl_2 \cdot 4H_2O$ with 100 ml of NaOH (using five different molarities, varying from 1.0 M to 12.5 M). This was followed by dropwise addition of 50 ml of 0.1 M H_2O_2. Therefore, the reacting solutions were prepared as follows:

(a) To prepare 100ml 0.1 M concentration of $FeCl_2 \cdot 4H_2O$:

→ Weight of $FeCl_2 \cdot 4H_2O$ = 0.1 M x 0.1 dm^3 x 198.8 g/mole

= 1.988 g

∴1.988 g of $FeCl_2 \cdot 4H_2O$ crystals were dissolved in 100 ml of deionized water to prepare 0.1 M of ferrous chloride solution.

(b) To prepare *y* M (Molar) concentration of NaOH in 100ml:

→ Weight of NaOH = *y* M x 0.1 dm^3 x 40.0 g/mole

∴The required weight of NaOH mini pearls to prepare base solutions with concentrations of 1.0 M, 2.0 M, 5.0 M, 10.0 M and 12.5 M are given in Table 3.1.

Table 3.1: Weight of NaOH mini pearls required to prepare various concentrations of alkali solutions.

Concentration of NaOH, *y* (M)	**Weight of NaOH (g)**
1.0	4.0
2.0	8.0
5.0	20.0
10.0	40.0
12.5	50.0

(c) To prepare 500 ml 0.1 M concentration of H_2O_2:

$$\rightarrow \quad \text{Volume of } H_2O_2 = \frac{0.1\,M \times 0.5\,dm^3}{8.821\,g/mole}$$

$$= 5.67 \text{ ml}$$

$\therefore$ 5.67 ml of H_2O_2 from the stock bottle was added to a 500 ml volumetric flask and topped up with dH_2O in order to prepare 500 ml of 0.1 M concentration.

3.4 Preparation of Zeolite-Iron Oxide (ZIO) Systems

The preparation procedure was done according to the following steps: firstly, 100 ml of 0.1 M $FeCl_2{\cdot}4H_2O$, 100 ml of 1.0 M NaOH and 500 ml of 0.1 M H_2O_2 were prepared. Two to three drops of dilute nitric acid (0.1 M) were added to the ferrous chloride solution to prolong the stability of the Fe(II) cations. Next, 30 ml of deionized water was added to 1 g of zeolite Na-Y powder. This suspension was gently stirred with a glass stirrer before being poured into the filter crucible. While the zeolite Y powder was settling into a layer at the bottom of the crucible, the vacuum pump was switched on so that the water was swiftly removed. This step was to ensure a closely-packed layer of zeolite in order to facilitate effective ion exchange of ferrous ions from $FeCl_2{\cdot}4H_2O$ with sodium ions in the zeolite.

Next, the ion-exchange process was initiated when the ferrous chloride solution was poured into the crucible. More deionized water was passed through the zeolite layer to wash off excess physically adsorbed ferrous ions on the external surfaces of the zeolites, with the vacuum pump switched on the entire time. The ion-exchange procedure and apparatus is shown schematically in Fig. 3.1.

After excess liquid is removed from the filter crucible, the remaining material was in the form of a paste. The zeolite paste now containing ferrous ions (z-Fe) was spooned out and placed in a 250 ml beaker mixed with about 30 ml of water for the following precipitation procedure. This beaker was placed on a hot plate and stirred

while 100 ml of 1.0 M NaOH solution was added. The mixture of z-Fe system and NaOH was slowly heated up to 60°C for 30 minutes. Then, 50 ml of 0.1 M H_2O_2 solution was added dropwise over a period of 20 minutes. The combined action of the NaOH, H_2O_2 and heat transformed the z-Fe system into the zeolite-iron oxide (ZIO) system. The heat was turned off and the mixture was left to stir for 20 hours.

The ZIO system was then washed thoroughly with deionized water for five times in the centrifuge (5000 rpm, 5 minutes) and then dried in the oven at 40°C. This temperature setting is chosen so that excess moisture can be removed but the heat is low enough so as not to facilitate any phase transformation in the ZIO systems. The precipitation procedure is shown in the schematic diagram in Fig. 3.2.

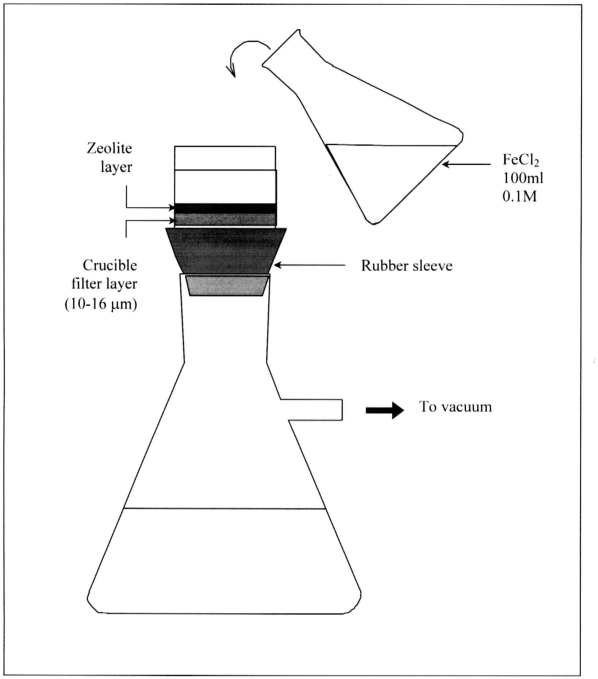

Fig. 3.1: The ion-exchange procedure.

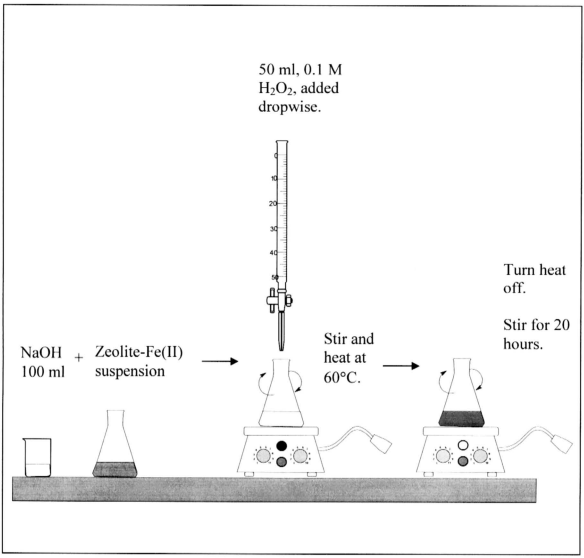

Fig. 3.2: The iron oxide precipitation procedure.

The experimental procedure was repeated using 2.0 M, 5.0 M, 10.0 M and 12.5 M NaOH solutions to yield 5 different samples for investigation. Table 3.2 shows the five samples of ZIO systems that were prepared with corresponding amounts of zeolite Y powder, ferrous chloride solution, NaOH and H_2O_2. The targeted variable in this set of experiments is the NaOH concentration, though another variable, the zeolite:ferrous chloride ratio also varies from 9.5 to 10.6. This varied ratio was unavoidable due to the experimental conditions because (1) $FeCl_2$ has to be freshly prepared for each sample as the solution becomes unstable after being exposed to air, and (2) the zeolite powder is extremely light and can float in the air, thus its container has to be quickly covered.

Table 3.2: Sample preparation of zeolite-iron oxide (ZIO) systems.

Sample	**Weight of zeolite (g)**	**$FeCl_2 \cdot 4H_2O$ concentration (M)**	**NaOH concentration (M)**	**H_2O_2 concentration (M)**
ZIO-1	1.00016	0.1054	1.0	0.1
ZIO-2	1.01965	0.1014	2.0	0.1
ZIO-3	1.03570	0.1006	5.0	0.1
ZIO-4	1.01736	0.1002	10.0	0.1
ZIO-5	1.07850	0.1017	12.5	0.1