Effect of preparation method on physicochemical properties of Fe/zeolite catalyst

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Abstract. A mesoporous zeolite silica alumina supported catalyst was impregnated with 3% Fe using different method of impregnation. This study focusing in finding the best impregnation method with the highest metal loaded and highly dispersion of impregnated metal. The impregnation methods carried out are wet impregnation, sono-chemical impregnation and point zero charge (PZC) impregnation. All prepared catalysts were analysed using AAS and FESEM to see the effective impregnation method. Based on the result, sono-chemical impregnation showed the highest actual Fe impregnated into the supported catalyst at 2.6 wt.% and 4.0 wt.% as detected by AAS and FESEM-EDX respectively.

1. Introduction
Catalyst able to speed up a reaction or process. Most industries sector nowadays chooses to incorporate a catalyst in their process to increasing the activity or selectivity of the reaction. The advances in catalyst preparation has prompted renewed interest in catalyst preparation and modification [1, 2]. One of the factors governing the activity of a catalyst is the metal – support interaction.

The advance and flexibility in metal - catalyst interaction has contributed to a widely potential application [1]. Capability of each prospect metal to enhance the activity of catalytic reaction have urged more study to be performed to observe the effect the metal – support catalyst interaction on the catalytic conversion [1-4]. The interaction of metal and the support has enhanced the activity, selectivity and the strength of the catalyst produce [3, 4]. Different metal would create different trait of interaction [2, 4].

Metal – support interaction can be achieved by impregnation method. Previous studies have stated that modification of supported catalyst by impregnation have brought up exceptional result based on the acidity of support interact with potential metal [1, 3]. Impregnation of metal on the catalyst support would produce catalyst with more reactivity and selectivity, which enhance the catalyst development process. Metal oxide can be impregnated to the support via various methods and different metal loading. In this paper, Fe/zeolite catalyst has been prepared via various impregnation methods to study its effect on the physicochemical properties of the catalyst.
2. Materials and methods

2.1. Materials
Commercial zeolite was purchased from ACS Materials, Inc. The type of zeolite used is not disclosed here due to our agreement with the funder of this research. General characteristics of the zeolite used are listed in Table 1. Iron (III) nitrate and other chemicals were purchased from Merck (99% purity grade).

| Characteristics                  | Value |
|----------------------------------|-------|
| SiO$_2$/Al$_2$O$_3$ Molar Ratio  | ~30   |
| Shape                            | Column (pelletized) |
| Dimension                        | Φ 2×2-10 mm |
| Pore Volume                      | $\geq$0.25 ml/g |
| Bulk Density                     | ~0.72 kg/l |
| Specific Surface Area            | $\geq$250 m$^2$/g |
| Pore Size                        | ~5 Å |
| Binder Type                      | Pseudo-Boehmite |
| Binder wt.%                      | 30 wt.% |

Table 1. Characteristic of zeolite support

2.2. Catalyst preparation
3 wt.% Fe/zeolite catalyst was prepared using various wet impregnation method. Sufficient amount of iron (III) nitrate was dissolved in deionized water to give 3 wt.% of Fe on zeolite support before zeolite was added to the aqueous iron (III) nitrate solution. The mixture was either left in water-bath shaker at medium speed for 4 hours at room temperature (WI shaker) or stirred at 100 rpm for 4 h at room temperature (WI stir) following the work done by Anita et al. [5]. Another mixture was sonicated using 20-kHz Q700 QSonica equipped with $\frac{1}{4}$” probe tip for 5 min (WI sonochemical) following the work reported by Zhang et al. [6]. The fourth mixture was impregnated using point zero charge (PZC) method via salt addition as reported by Farooq et al. [7] and Mahmood et al. [8].

In PZC method, the PZC of the support was determined by salt addition method with 0.1 M ammonia solution as an electrolyte buffer where the deionizer water was first preheated to 30 – 60 °C to eliminate CO$_2$. 40 ml of the electrolyte was added to 0.2 g of catalyst and pH of the suspension was adjusted using 0.1 M nitric acid or 0.1 M sodium hydroxide to achieve the desired pH for analysis. The catalyst was left on shaker bath at medium speed at room temperature for 24 h. The initial and final pH was recorded using Ohaus® Starter 3100 bench pH meter and pH changes ($\Delta$ pH) is plotted. Based on the plotted $\Delta$ pH graph, pH 6 was chosen as the working pH value for PZC impregnation. All catalysts prepared were then dried at 120 °C for 24 h and calcined at 550 °C for 6 h. The overall procedure in preparation the catalyst is illustrated in Figure 1.
2.3. Catalyst characterization analysis

Atomic absorption spectrometry (AAS) was used to measure the concentrations of elements. The analysis was carried out by dissolving the sample in HCl and H₂SO₄ then the solid residue was filtered. The concentration of the Fe was determined by plotting the Fe standard calibration graph obtained AAS and the concentration of Fe present in the sample is calculated from the result obtained. Field Emission Scanning Electron Microscope (FESEM) was used to provide the morphology of the crystallization of catalyst. EDX mapping analysis was programmed to observe the metal distribution on the zeolite support.

3. Result and discussion

The salt addition of Fe to the zeolite support catalyst change the pH of the mixture solution that can be seen in Figure 2. The ∆pH is plotted against the initial pH values and the ∆pH resulted to zero is the indication of the PZC value of the catalyst. From the graph, the PZC value of the catalyst support is 4.3 almost the same as reported in previous study [9, 10]. The pH 6 is chosen due to the pH value above pH 4.3 will promote Fe³⁺ to deposited easily on the surface of the zeolite support as at this state the surface of zeolite support is negatively charged.
Impregnation of metal on catalyst support will modify the functionality and selectivity of the catalyst [1-4, 11], therefore, it is essential to really know the actual Fe concentration in the catalyst for the catalyst to perform well. Theoretical and actual Fe loading was determined by AAS and FESEM-EDX analyses. AAS analysis is more accurate compared to FESEM-EDX as AAS measured the concentration of the sample in substance rather than FESEM-EDX determining the concentration based on the surface exposure.

From Table 2, the highest actual iron concentration impregnated into catalyst support is attained using sono-chemical method. The sono-chemical method allows the metal to be impregnated into the catalyst support by external forces which enhances the binding of metal to the framework of the catalyst support. Theoretical Fe was determined from the amount of Fe salts used for the impregnation while actual Fe loading was determined using AAS and FESEM-EDX as shown in Table 2.

The actual Fe concentration for WI Sonochemical is 4.0 wt.% measured by FESEM doesn't correlate well with the theoretical amounts of Fe (3 wt.%) used for catalyst preparation. Heterogeneous catalysts tested using FESEM-EDX are influenced by the penetration depth of the electron beam on the layer thickness, Fe cluster size, surface coverage, preparation performance and, under certain conditions. The accuracy of FESEM is strongly influenced by morphological effects and heterogeneity of the catalyst coverage of the analysed samples.

However, AAS measured 2.6 wt.% Fe content which is slightly correlate with the theoretical amounts of Fe (3 wt %) due to the bulk sample is atomized, and a beam of electromagnetic radiation emitted from excited Fe atoms is passed through the vaporized sample. Furthermore, AAS accurately measure all the element present in the sample and it measures down to parts per billion of a gram of Fe content in catalyst.

Table 2. Theoretical and actual Fe content in the Fe/zeolite catalyst.

| Impregnation method | Theoretical Fe conc. (wt.%) | Actual Fe conc. (wt.%) | AAS | FESEM-EDX |
|---------------------|-----------------------------|------------------------|-----|-----------|
| WI shaker           | 3                           | 1.8                    | 1.1 |           |
| WI stir             | 3                           | 2.3                    | 2.2 |           |
| WI sonochemical     | 3                           | 2.6                    | 4.0 |           |
| PZC                 | 3                           | 2.4                    | 1.8 |           |
Figure 3. shows the morphology and mapping of the Fe/zeolite catalysts prepared via various wet impregnation method. FESEM-EDX allows us to study the surface morphology and elemental composition of the catalyst. In Figure 3, all the catalyst seems to have an irregular shape and porous zeolite structure. The FESEM micrograph also showed irregular shape particles were found on the surface of all catalysts. The particles deposited on the surface were measured to be around 25 – 50 nm.

The Fe metal distribution in the samples is uniformly distributed and evenly disperses which can be clearly seen from the mapping image in Figure 3. From Figure 3(c) showed that WI sonochemical have more even distribution of Fe compared to other impregnation methods. From the observation, the distribution of Fe in the catalyst can be sorted from highest to lowest Fe content as WI sonochemical > WI stir > PZC > WI shaker.

![Figure 3. FESEM images with mapping of Fe/zeolite catalyst prepared via different preparation method at 10kX magnification. The illustrations represented the impregnation method applied (a) WI shaker (b) WI stir (c) WI sonochemical (d) PZC; The mapping for Fe is illustrated by purple and yellow mapping image.](image-url)
4. Conclusion
Catalyst preparation method is one of the crucial steps in producing an efficient catalyst. From our work, WI sonochemical method is the best impregnation method to give Fe loading closest to the theoretical loading of 3.0 wt.% which is 2.6 wt.% and 4.0 wt.% as determined using AAS and FESEM-EDX method respectively.

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