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Comparison of Synthesis Techniques for Supported Iron Nanocatalysts

¹S.F.H. Tasfy, ²N.A.M. Zabidi and ¹D. Subbarao

¹Department of Chemical Engineering,

²Department of Fundamental and Applied Sciences, Universiti Teknologi PETRONAS,
Bandar Seri Iskandar, 31750 Tronoh, Perak, Malaysia

Abstract: Iron-based catalyst is the most common catalyst for Fischer-Tropsch Synthesis (FTS), which is a process to synthesize transportation fuel and chemicals feedstock from the syngas. The effect of synthesis technique, iron loading and catalyst supports on the physicochemical properties of iron-based catalyst was investigated. Impregnation and precipitation methods were used to synthesize the supported iron-based nanocatalysts containing various iron loadings. Silica and alumina silica were used as catalyst supports to modify the catalyst properties in producing well defined phases. The supported iron nanocatalysts were characterized using N₂ physical adsorption, Field Emission Scanning Electron Microscopy (FESEM), Transmission Electron Microscopy (TEM) and Temperature-Programmed Reduction (TPR). For the catalysts prepared via impregnation method, the surface area remained at 23 m² g⁻¹ for catalyst containing different iron loading. However, for those prepared via the precipitation method, the surface area of the catalyst increased with increasing iron loading. Precipitation method resulted in highly agglomerated iron nanoparticles. The 6% Fe SiO₂ nanocatalyst prepared via impregnation method resulted in relatively small and uniform dispersion of iron nanoparticles. However, bimodal distribution was observed for the 10 and 15% Fe SiO₂. Similar trend was observed when Al₂O₃-SiO₂ was used as a catalyst support. H₂-TPR profiles for Fe SiO₂ nanocatalysts synthesized via impregnation showed two reduction stages while those prepared using precipitation method resulted in three reduction peaks. The TPR peak positions remained the same for various iron loadings.

Key words: Fischer-Tropsch synthesis, iron-based catalysts, impregnation, precipitation, silica support, alumina-silica support.

INTRODUCTION

Due to the depletion of oil reserves and unpredictable price of petroleum fuel derived from crude oil, it is necessary to develop alternative method for synthesizing liquid fuels derived from other abundant energy sources such as coal, biomass and natural gas. Fischer-Tropsch Synthesis (FTS) has been recognized as a promising route to produce liquid fuels and valuable chemical feedstock to meet the continuously increasing demand for these products (Xiang *et al.*, 2007). Fischer-Tropsch synthesis is a polymerization process in which a monomer produced on the surface is added stepwise to a growing aliphatic chain. The chemistry of FTS is rather complex and the reaction has a high exothermicity. Two types of reactions take place at the FTS are FT and Water-Gas-Shift (WGS) reactions. The most common catalysts used for FTS are ruthenium, cobalt, iron and nickel. Although, these metals are considered as the most common active component for FTS only iron and cobalt catalysts appear to be economically feasible on an industrial scale

(Khodakov, 2009). Cobalt-based catalysts are widely investigated for the syngas which is derived from natural gas with high H₂/CO ratio. Meanwhile, iron-based catalyst is attractive due to their high FTS activity for the low H₂/CO ratio as well as their water-gas shift reactivity (Kalakkad *et al.*, 1995), and also due to their low cost (Li *et al.*, 2006). In order to improve the performance of the catalyst many attempts have focused on the addition of chemicals such as promoters, supports and many other additives. Li *et al.* (2006) have reported that silica which was used as a support will affect the properties of the precipitated iron-based catalyst by facilitating the dispersion of Fe₂O₃. In contrast, silica suppresses the carburization, resulting in the weak CO adsorption and decreases the FT activity as well as improving the stability and the selectivity of light hydrocarbon. The optimization of chemical, physical, mechanical and catalytic properties requires a careful choice of the components such as active phase, promoter and support for the synthesis of the catalyst which determines catalyst activity and product selectivity

(Yamada *et al.*, 2002). Pirola *et al.* (2009) found that the CO conversion and heavy hydrocarbon selectivity increase with increasing the iron loading and also in the presence of promoter, accordingly the performance of the FT synthesis was enhanced due to increasing iron loading. Since iron catalysts have much potential for the selective hydrogenation of CO to the hydrocarbon with a low molecular weight, this potential can be enhanced by medium acidic support or addition of promoters (Snel, 1989). Tsubaki *et al.* (2005) reported the influence of alumina-silica on the performance of the FT catalyst and they showed that alumina-silica support improved the dispersion of the metal and increased the reduction temperature and enhanced the FT activity. The method of preparation is known to have a profound influence on the catalytic properties of supported catalyst. It influenced the degree of dispersion and interaction between the metal and support (Snel, 1989).

The aim of this study is to develop iron-based nanocatalysts for FTS by synthesizing a series of iron nanoparticles catalyst with different iron loading supported on silica or alumina-silica supports via impregnation and precipitation methods. The effect of synthesizing techniques, supports and iron loading on the property of the catalysts have been investigated using N₂ physical adsorption, FESEM, H₂-TPR and TEM analyses.

MATERIALS AND METHODS

Iron-based catalyst was synthesized using two preparation methods, namely impregnation and precipitation methods. Different metal loading (6, 10 and 15 wt%) was applied over two types of supports. The catalyst supports used were commercial silica (supplied by aerosilOX05-evonik industries) and synthesized alumina-silica (Al₂O₃-SiO₂).

Preparation of Al₂O₃-SiO₂ support: Al₂O₃(NO₃)₃·9H₂O was dissolved in glycol and stirred at 80°C for 1h. The alumina solution was added to commercial silica (aerosilOX05-evonik industries, BET 40.8 m² g⁻¹) then the mixture was stirred for 12 h. The sample was dried at 120°C for 12 h and calcined at 600°C for 4 h (Tsubaki *et al.*, 2005).

Incipient wetness impregnation method: Commercial silica and synthesized alumina-silica support were impregnated with an aqueous solution containing Fe(NO₃)₃·9H₂O (0.5 M). Then the mixture was stirred for 24 h. Impregnated sample was dried at 120°C for 12 h and calcined in air flow at 600°C for 4 h (Saib *et al.*, 2006).

Precipitation method: A solution containing Fe(NO₃)₃·9H₂O (0.5 M) was precipitated at pH 9-10 and 80°C by using ammonia solution as the precipitating agent. The sample was washed by deionized water several times and filtered. The washed precipitate was added to the support and stirred over night then dried at 120°C for 12 h and calcined for 4 h at 600°C in flowing air (Hayakawa *et al.*, 2007).

Catalyst characterization: Total surface area, pore volume and average pore size were determined using micromeritics (ASAP 2000) adsorption equipment based on BET adsorption. N₂ gas was used as the adsorbate (Webb and Orr, 1997). Field-Emission Scanning Electron Microscopy (FESEM) was used to observe the morphology of the catalyst and to verify the metal dispersion. The particle size was analyzed using Transmission Electron Microscopy (TEM). H₂ Temperature-Programmed Reduction (H₂-TPR) profiles of calcined catalyst were measured using a micromeritics TPD/R/O 1100 system. A 5% hydrogen in nitrogen gas was used to record the TPR profile. The samples (20 mg) was placed in a quartz cell and heated under flowing nitrogen from 40 to 250°C at the rate of 10°C min⁻¹. The flow was then switched to 5%H₂/N₂ and the temperature was increased to 900°C at the rate of 10°C min⁻¹ and held for 2 h. A Thermal Conductivity Detector (TCD) was used to determine the concentration of H₂ and H₂ chemisorptions uptakes were determined by integrating the area of H₂-TPR curves (Jozwiak *et al.*, 2007).

RESULTS AND DISCUSSION

Textural properties of the catalysts: The textural properties of the support and supported iron-based catalysts prepared by impregnation and precipitation methods are shown in Table 1. Surface area, pore volume and average pore size were obtained via N₂ physical

Table 1: The textural properties of the support and supported iron-based catalysts

Sample	% loading	BET surface area (m ² g ⁻¹)	Pore volume (cc g ⁻¹)	Average pore size (Å)
SiO ₂ ^A	-	40.86	0.094	91.79
Al ₂ O ₃ -SiO ₂ ^B	10%Al ₂ O ₃ -SiO ₂	54.96	0.173	125.96
Fe/SiO ₂ ^C	6% Fe/SiO ₂	23.18	0.093	161.15
Fe/SiO ₂ ^C	10%Fe/SiO ₂	23.82	0.088	147.85
Fe/SiO ₂ ^C	15%Fe/SiO ₂	23.98	0.071	144.12
Fe/SiO ₂ ^D	6% Fe/SiO ₂	40.57	0.118	116.31
Fe/SiO ₂ ^D	10%Fe/SiO ₂	43.11	0.140	130.18
Fe/SiO ₂ ^D	15%Fe/SiO ₂	45.64	0.175	134.61
Fe/Al ₂ O ₃ -SiO ₂ ^C	6%Fe/Al ₂ O ₃ -SiO ₂	47.95	0.163	171.68
Fe/Al ₂ O ₃ -SiO ₂ ^C	10%Fe/Al ₂ O ₃ -SiO ₂	53.00	0.214	184.28

A: commercial silica (aerosilOX05-evonik industries). B: synthesized alumina-silica support C: catalyst prepared by impregnation method. D: catalyst prepared by precipitation method

adsorption analyses. The result shows that adding alumina to the silica support increased the BET surface area from 40.86 to 54.96 m² g⁻¹, due to increase in the porosity and the pore size of the mixed support. Silica-supported iron nanocatalysts synthesized via impregnated method have the same BET surface area (23 m² g⁻¹) for different Fe loading (6, 10 and 15%). In contrast, the precipitated catalyst showed increasing surface area with increasing the Fe loading. The silica-supported iron nanocatalysts prepared via precipitation method have higher surface areas and smaller pore size compared to those prepared by the impregnation method. However, iron-based catalysts supported by Al₂O₃-SiO₂ support observed higher surface area comparing to those supported by SiO₂.

Surface morphology: Figure 1 and 2 show the morphology of Fe nanoparticles on SiO₂ support prepared via impregnation and precipitation method, respectively. Spherical nanoparticles with wide range of particle size are shown by using FESEM technique. Highly agglomerated iron nanoparticles were obtained for the catalysts synthesized by precipitation method compared with impregnation. According to Pirola *et al.* (2009) SEM results shows a well dispersed of the Fe particles on the support surface even in the high Fe charge, where as the aggregation and distribution of the Fe particles increase due to increasing of the iron loading.

Particle size and distribution: Figure 3 shows the TEM images of catalyst prepared via impregnation method. The

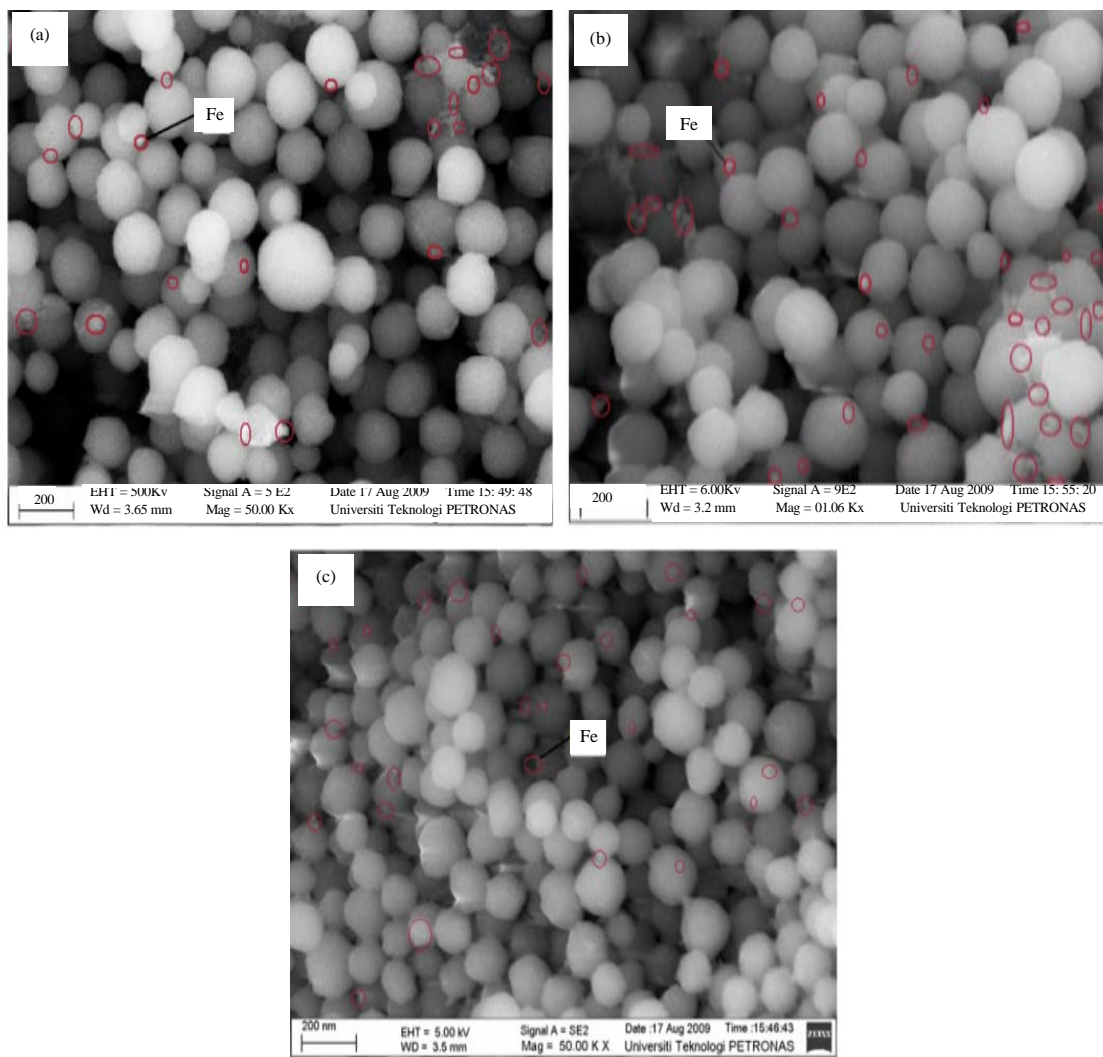


Fig. 1: FESEM images of (a) 6%, (b) 10% and (c) 15% Fe SiO₂ prepared by impregnation method

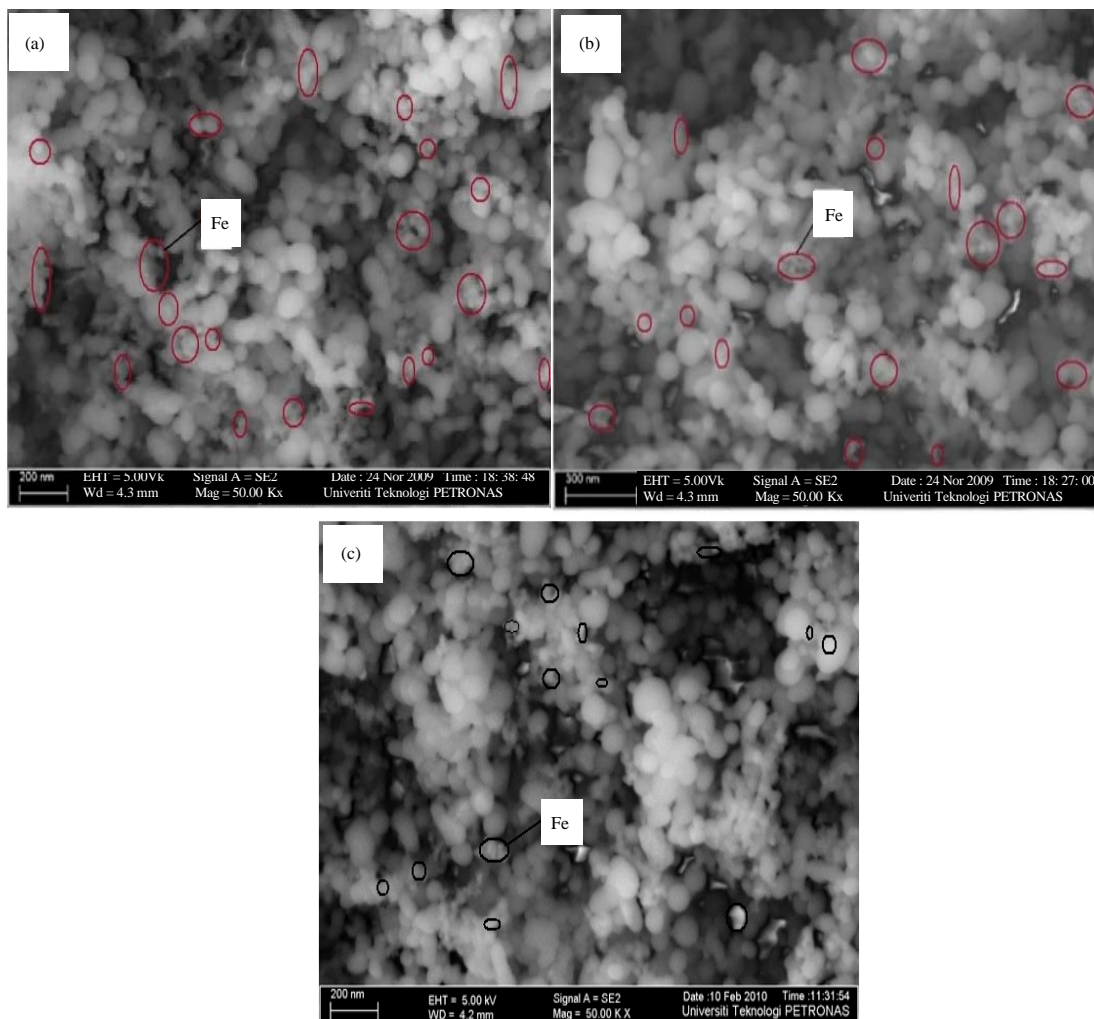


Fig. 2: FESEM images of (a) 6% (b) 10% (c) 15% Fe SiO₂ prepared by precipitation method

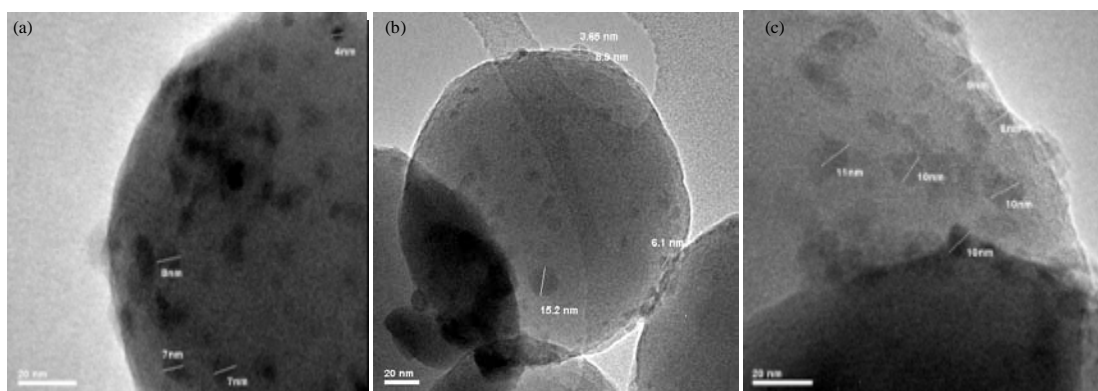


Fig. 3: TEM images for (a) 6 (b) 10 (c) 15% Fe on SiO₂ prepared by impregnation method

results show that the catalyst particles size increased with increasing Fe loading and it ranged from 4-14 nm for

6%Fe, 6-20 nm for the 10% Fe and 9-20 nm for the 15% Fe loading with 8.6±1.07, 12.6±1.3 and 13±1.2 nm average

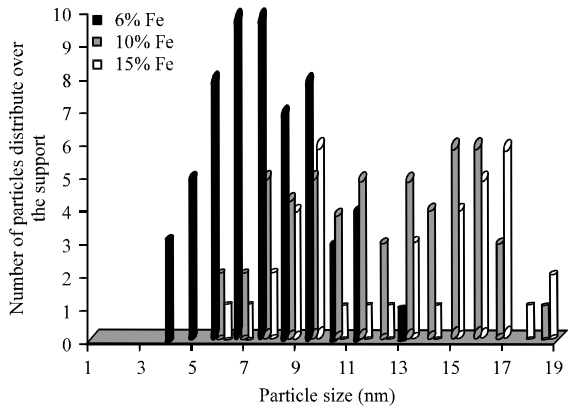


Fig. 4: Particle size distribution for 6, 10 and 15% Fe on SiO₂ support prepared by impregnation method

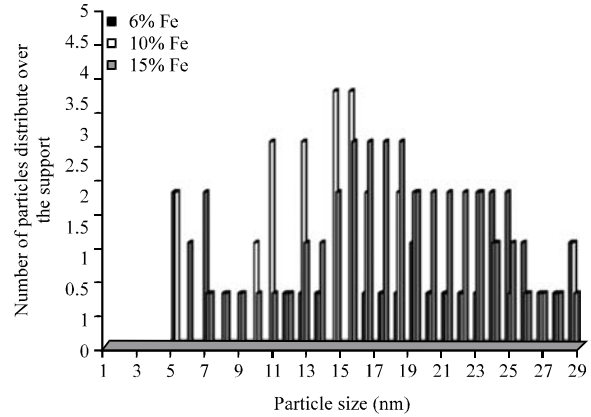


Fig. 6: Particle size distribution for 6, 10 and 15% Fe on SiO₂ support prepared by precipitation method

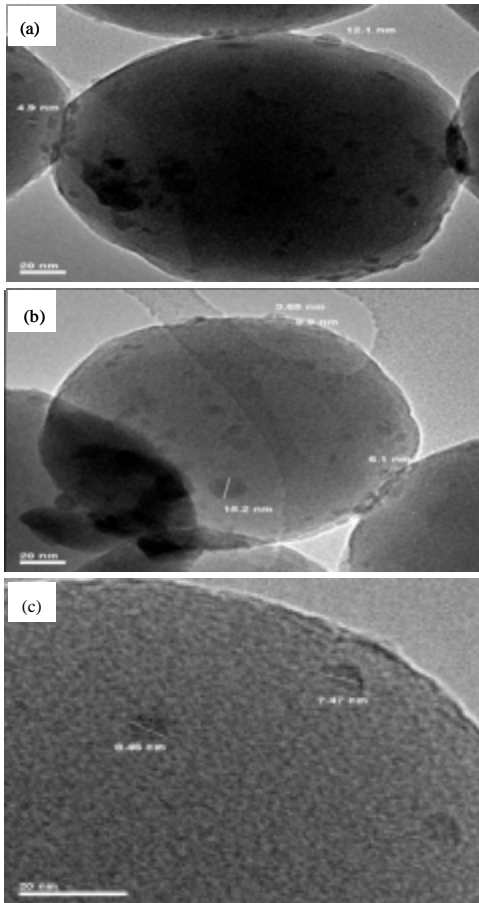


Fig. 5: TEM images for (a) 6 (b) 10 and (c) 15% Fe SiO₂ prepared by precipitation method

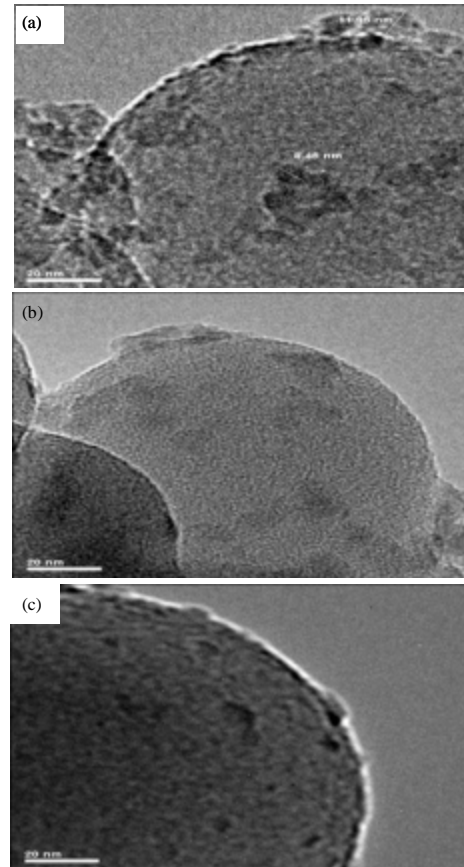


Fig. 7: TEM images for (A) 6% (B) 10% (C) and 15% Fe Al₂O₃-SiO₂ catalysts prepared by impregnation method

particles size, respectively. More uniform distribution of the iron nanoparticles was observed for the 6% Fe

compared to those of the 10 and 15% Fe as shown in Fig. 4. Catalysts which were prepared by precipitation

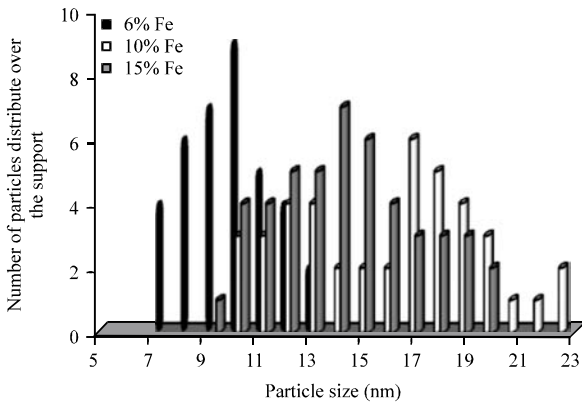


Fig. 8: Particle size distribution for 6, 10 and 15% Fe on $\text{Al}_2\text{O}_3\text{-SiO}_2$ support prepared by impregnation method

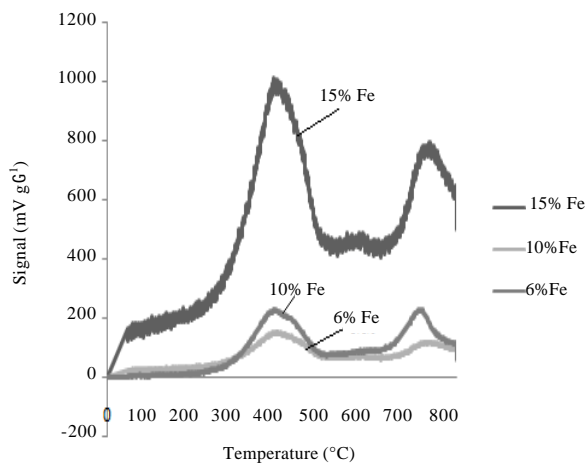


Fig. 9: TPR for Fe SiO_2 catalysts prepared by impregnation method

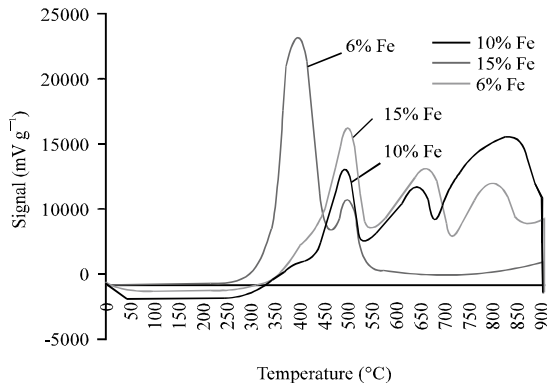


Fig. 10: TPR for Fe SiO_2 catalysts prepared by precipitation method

method have broader size distribution and larger iron nanoparticles compared to those prepared by the impregnation method. As shown in Figure 5, the particle size of 6% FeSiO_2 catalyst prepared by precipitation method ranged between 5-27 nm with 19.3 ± 6.6 nm average particles size and for the 10% it ranged from 9-30 nm with 17.7 ± 7.3 nm average size. Figure 6 shows that the precipitation method resulted in a wider particle size distribution compared to those synthesized via the impregnation method.

Figure 7 shows the TEM images of iron supported on $\text{Al}_2\text{O}_3\text{-SiO}_2$ and it obtain 7-13 nm particle size for 6% Fe, 10-23 nm for 10% Fe and 9-20 nm for 15% with 10 ± 2 , 17.8 ± 5.3 and 14.5 ± 3.3 nm as an average particles size, respectively. The particle size distribution for catalyst supported by $\text{Al}_2\text{O}_3\text{-SiO}_2$ (Fig. 8) has similar trend as those obtained on the SiO_2 support.

Temperature-Programmed Reduction (TPR): Reduction behavior of the calcined catalyst was studied by H_2 -TPR. The H_2 -TPR profiles of the catalysts are shown in Fig. 9 and 10. For most of the unsupported iron-based catalysts, the reduction occurs in two distinct stages at the temperature range between 350-500°C. The first stage ascribed to the transformations of $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$, whereas the second stage represents the transformation of $\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$ (Jozwiak *et al.*, 2007; Wan *et al.*, 2006; Jin and Datye, 2002). The TPR results for iron catalyst supported on silica suggest that the addition of SiO_2 increased the reduction temperatures of the iron for both transformation steps this result was in line with those reported by Li *et al.* (2008), in which the increase of the SiO_2 content suppresses the reduction due to stabilization of Fe_3O_4 phase. The TPR curve (Fig. 9) shows two reduction peaks for impregnated Fe/SiO_2 catalysts, the first one from 320-460°C for transforming the $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ and the second stage was observed at a higher temperature from 660-780°C related to transformation of the magnetite phase to metallic phase ($\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$) (Li *et al.*, 2006). However, for the catalyst prepared using precipitation method, three reduction peaks were observed (Fig. 10) for the 6, 10 and 15% Fe SiO_2 catalysts. The reduction of $\text{FeOOH} \rightarrow \text{Fe}_2\text{O}_3$ was observed at the temperature range from 420-540°C. The second peak at 580-660°C was for reduction of $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ and the third peak, which appeared at 680-900°C was related to the production of metallic phase (Fe) from Fe_3O_4 .

CONCLUSION

Supported nanoparticles iron-based catalysts with different iron loading on SiO_2 and $\text{Al}_2\text{O}_3\text{-SiO}_2$ were

prepared by impregnation and precipitation methods. The results show that supported iron-based catalyst prepared by impregnation method has a lower surface area and bigger pore size than those prepared by precipitation method. The surface areas of impregnated catalysts did not vary with iron loading. Highly agglomerated iron nanoparticles were observed for the precipitated catalysts and the catalysts supported by $\text{Al}_2\text{O}_3\text{-SiO}_2$ compared to those synthesized via the impregnation method supported by SiO_2 . The impregnation method enhanced the distribution of iron nanoparticles over the support and revealed smaller particle size compared to the precipitated catalysts. TEM results show similar trend for SiO_2 and $\text{Al}_2\text{O}_3\text{-SiO}_2$ supports, nevertheless, iron particle size increased with increasing iron loading for both preparation and impregnation methods. TPR results show that Fe/SiO_2 prepared by impregnation method has two reduction stages which were not affected by Fe loading while precipitation method resulted in formation of iron oxides particles which were reduced at higher temperature compared to those of the impregnation method.

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