Synthesis and Characterization of Silica-supported Iron Nanocatalyst by Modified Colloidal Method

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Abstract: Silica-supported iron nanocatalysts for Fischer-Tropsch Synthesis (FTS) were prepared using the modified colloidal method in the presence of surfactants in an organic medium. The iron loading on silica support was varied at 3, 5 and 6 wt.%. The samples were characterized by XPS, TPR and TEM. The presence of FeO on the silica support was confirmed by XPS. TPR analysis showed that the increase in Fe loading caused the first reduction temperature of the nanocatalysts to shift to a higher temperature. TEM analysis revealed that the iron nanoparticles were not uniformly distributed on the silica support. The size of iron nanoparticles ranged from 4 to 20 nm. For the 3 and 5 wt.% Fe/SiO₂, the size of the iron nanoparticles were mostly in the range of 1-5 nm, whereas for the 6 wt%, most of the iron nanoparticles (74%) were in the range of 6-10 nm.

Key words: Silica support, iron nanocatalyst, XPS, TPR, TEM

INTRODUCTION

Fischer-Tropsch Synthesis (FTS) has been recognized as an important technology in the production of liquid fuels and chemicals from syngas derived from coal, natural gas, and other carbon-containing materials (Zhao et al., 2008). The main aim of FTS research is to improve the selectivity for C₅ hydrocarbons and to decrease the selectivity for methane, and the key to realizing this aim is to develop FT catalyst with high activity and selectivity (Lihong et al., 2007).

Although several metals (including Co, Ni, and Ru) have been considered as the most commonly active component for FTS catalysts, iron-based catalysts are widely used because of the high FTS activity, low cost, flexible product distribution and favorable engineering characteristics (Ding et al., 2008). The properties of iron nanoparticles depend on its size; smaller particles should improve the kinetics of the reactions (Huber, 2005).

In this study, iron nanocatalyst was prepared by the modified colloidal method. The modified colloidal method is the preferred catalyst preparation method because it can result in nanocatalyst particle having size 4 to 15 nm, which is expected to have high activity and selectivity for FTS (Zabidi, 2007). Colloidal synthesis has been widely used as an efficient route to control metal particle size and shape, crystallinity and crystal structure (Khodakov et al., 2007). Colloids are synthesized in the presence of surfactants which disperse and stabilize the nanoparticles in an organic solvent. Some of the approaches include polylol method, ethylene glycol method, modified coordination capture method and pseudo-colloidal method. The polyl method involves heating a mixture of catalyst precursor in surfactants, such as oleic acid and oleyl amine in high-boiling solvent such as diphenyl ether (Zabidi, 2007). The size of the nanoparticles is controlled by changing the concentration of the precursor, the amount and type of surfactant, the aging time and temperature of the reaction.

High temperature alcohol reduction of iron(III) acetylacetonate metal precursor resulted in monodisperse iron nanoparticles. This synthesis process is also called “heating-up” process (Khodakov et al., 2007). Another synthesis method that produces uniform nanocrystals that is comparable to the “heating-up” process is called the “hot injection” method. The “hot injection” method induces high supersaturation and leads to fast homogeneous nucleation reaction followed by diffusion-controlled growth process, which control the particle size distribution.

The objective of this research was to prepare a spherical model nanocatalyst comprising iron nanoparticles supported on silica spheres. This report will highlight the effect of iron loading on the properties of the
MATERIALS AND METHODS

Synthesis of iron nanocatalyst: The iron nanocatalyst was prepared by the modified colloidal method (Zabidi, 2007). The experimental setup used in synthesizing the SiO₂-supported iron nanocatalyst is shown in Fig. 1. Silica (SiO₂) spheres (BET surface area: 23.6 m²/g, pore volume: 0.14 m³/g) were synthesized using the Stöber method. The SiO₂ spheres were added to a surfactant mixture (designated as mixture A) containing oleic acid, oleyamine, cyclohexane and then placed in a bath sonicator for 3 h. Mixture A was poured into the multi-neck reaction vessel and heated to 265°C using a digital heater controller (Thermo Fischer Scientific EM 0100/CE) under nitrogen flow. The slurry was stirred at 200 rpm using a mechanical stirrer (Heidolph RZR 2021) throughout the synthesis period.

Another mixture (designated as mixture B) was prepared by mixing Fe (acac), 1, 2 hexanecodimethyl, oleic acid, oleyamine, and phenyl ether. The amount of Fe(acac)₃ was varied according to the desired iron loading (3, 5 and 6 wt.%). The molar ratio of Fe (acac)₃ to surfactant was kept at 1:18. Mixture B was placed in the bath sonicator for about 20 min to prevent crystallization of the phenyl ether solvent.

Mixture B was added dropwise to mixture A once the temperature of mixture A reached 150°C. The resultant black mixture was heated until the temperature reached 265°C. When the temperature reached 265°C, the mixture was heated for another hour. Then, the black mixture was cooled under nitrogen flow until the temperature decreased to 90°C. Ethanol was then added to the cooled reaction mixture to precipitate the nanoparticles. The solid was separated by centrifugation at 7000 rpm for 90 min. The precipitates obtained after the centrifugation was calcined in air at 450°C for 2 h in a furnace.

Characterization technique

XPS analysis: Surface analysis was conducted using XPS (Thermo Scientific K alpha) equipped with monochromatized Al Kα X-ray source and chaneltron detector. Analysis was carried out at vacuum <10⁻⁷ Torr. Powdered samples were placed in the holes of the sample holder block and scanned at pass energy of 50.0 eV.

TPR analysis: TPR analysis was conducted using TPD/R/O 1100 (Thermo Electron) to determine the reduction profile of the catalysts. A flow of 5%H₂/95%N₂, maintained at 50 cc min⁻¹ was used as the reducing gas. Typically, 0.1 g samples were reduced using 5%H₂/95%N₂ and heated to 800°C at a rate of 5°C min⁻¹.

TEM analysis: TEM analysis was conducted to observe the distribution of iron nanoparticles on the SiO₂ support. TEM images were obtained using Philip Tecnai 20 with accelerating voltage of 200 kV.

RESULTS AND DISCUSSION

XPS analysis: Figure 2 shows the XPS spectra of the Fe 2p region for the 3 and 5 wt.% Fe/SiO₂ nanocatalysts. The binding energies of the Fe 2p peaks are shown in Table 1.

The XPS results show that the Fe 2p₁/₂ peak was more intense than that of the Fe 2p₃/₂ peak. This is because of the spin orbit (j-j) coupling; Fe 2p₁/₂ has degeneracy of
Table 1: Binding energies for Fe 2p peaks

<table>
<thead>
<tr>
<th>Samples</th>
<th>Binding energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe 2p$_{3/2}$</td>
</tr>
<tr>
<td>3 wt.% Fe/SiO$_2$</td>
<td>725.1</td>
</tr>
<tr>
<td>5 wt.% Fe/SiO$_2$</td>
<td>725.3</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>724.1</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>724.6</td>
</tr>
</tbody>
</table>

$^1$Yamashita and Hayes (2008)

Table 2: Binding energy of O 1s for Fe/SiO$_2$ nanocatalyst

<table>
<thead>
<tr>
<th>Samples</th>
<th>Binding energy (eV) for O 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 wt.% Fe/SiO$_2$</td>
<td>533.0</td>
</tr>
<tr>
<td>5 wt.% Fe/SiO$_2$</td>
<td>533.1</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>527.0</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>531.0</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>531.5</td>
</tr>
</tbody>
</table>

$^1$Yamashita and Hayes (2008), $^2$Mekki (2005)

Fig. 3: XPS spectra of O 1s for 3 and 5 wt.% Fe/SiO$_2$ nanocatalyst

four states whilst Fe 2p$_{3/2}$ has only two states (Yamashita and Hayes, 2008). The peak positions of Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ for the Fe$_2$O$_3$ are 710.6 (SD = 0.05) and 724.1 eV (SD = 0.07), respectively (Yamashita and Hayes, 2008). For Fe$_3$O$_4$, the binding energies reported in the literature are 711.0 (SD = 0.01) and 724.6 (SD = 0.17) for Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$, respectively (Yamashita and Hayes, 2008). The peak positions of Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ obtained for the Fe/SiO$_2$ samples were in the range of Fe$_2$O$_3$ peaks reported in the literature. The 0.8 eV shift between the experimental binding energy of Fe 2p$_{3/2}$ and that of the literature value could be due to the metal–support interaction since the binding energy reported in the literature is for the unsupported Fe$_2$O$_3$.

Figure 3 shows the XPS spectra of O1s for Fe/SiO$_2$ nanocatalysts and the binding energies are shown in Table 2.

Table 3: Reduction temperatures of Fe/SiO$_2$ nanocatalysts

<table>
<thead>
<tr>
<th>Wt.%</th>
<th>Fe$_2$O$_3$ → Fe$_3$O$_4$</th>
<th>Fe$_3$O$_4$ → FeO</th>
<th>FeO → Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>373</td>
<td>Not detected</td>
<td>610</td>
</tr>
<tr>
<td>5</td>
<td>378</td>
<td>457</td>
<td>595</td>
</tr>
<tr>
<td>6</td>
<td>379</td>
<td>422</td>
<td>618</td>
</tr>
</tbody>
</table>

$^1$Yu et al. (2008)

Fig. 4: TPR profiles for 3, 5 and 6% Fe/SiO$_2$

As shown in Table 2, the binding energy of O 1s for both Fe/SiO$_2$ samples was 533 eV. The O 1s peak was contributed by both iron oxide and the silica support (SiO$_2$). From literature, the O 1s binding energy value for Fe$_2$O$_3$ is 531 eV while that of Fe$_3$O$_4$ is 527 eV (Yamashita and Hayes, 2008). Meanwhile, the binding energy value for O 1s of SiO$_2$ is 531.5 eV (Mekki, 2005). The shift in binding energy for O 1s peak between the SiO$_2$-supported Fe catalyst and that of Fe$_3$O$_4$ could be due to the strong Fe-SiO$_2$ interaction.

**TPR analysis:** Figure 4 and Table 3 show the results of TPR analysis for 3, 5, and 6 wt.% Fe/SiO$_2$ nanocatalysts. As shown in Fig. 4, the TPR profiles of the three nanocatalysts show two distinct reduction stages in the temperature range of 370-640°C. The first reduction stage, containing two partially overlapped peaks, can be assigned to the transformations of Fe$_3$O$_4$ → Fe$_2$O$_3$ and Fe$_2$O$_3$ → FeO (Yu et al., 2008). The second reduction stage can be assigned to the transformation of FeO → Fe, which is the reduction of Fe$_2$O$_3$ to γ-Fe via wüstite (FeO) as an intermediate (Yu et al., 2008). The TPR results were in agreement with the XPS results, which confirmed the presence of Fe$_3$O$_4$.

As shown in Table 3, the increase in Fe loadings caused the first reduction temperature of the nanocatalysts to shift to higher temperature. However, increase of Fe loadings did not strongly influence the reduction of Fe$_2$O$_3$ → FeO and FeO → Fe as the thermodynamics of the process involved the nucleation of new crystal structures instead of H$_2$ dissociation steps that control the reduction rates at higher temperatures (Pour et al., 2008).
Fig. 5: TEM image of 3% Fe/SiO₂

Fig. 6: TEM image of 5% Fe/SiO₂

Fig. 7: TEM image of 6% Fe/SiO₂

Fig. 8: Size distribution of iron nanoparticles for 3, 5 and 6 wt.% FeSiO₂

of the surface of SiO₂ support remain bare, indicating uneven deposition of iron nanoparticles on the support. Figure 8 shows the histogram of the size distribution of iron nanoparticles on silica support for the three samples prepared in this study.

The size of the iron nanoparticles for the 3 and 5 wt.% Fe/SiO₂ were mostly in the range of 1-5 nm (54% for 3 wt.% Fe/SiO₂ and 45% for 5 wt.% Fe/SiO₂), meanwhile for the 6 wt.% Fe/SiO₂, the size of the iron particles were mostly in the range of 6-10 nm (74%). The 6 wt.% Fe/SiO₂ had a narrower particle size distribution compared to those of 3 and 5 wt.% Fe/SiO₂ samples. The target iron particle size is between 4-10 nm. Therefore, it can be concluded that the size of iron nanoparticles obtained from all the three catalysts synthesized in this work were in the target range. The 6 wt.% Fe/SiO₂ nanocatalyst was the best catalyst model amongst the three samples investigated in this work because it showed a better particle size distribution compared to the other two samples.

CONCLUSION

Silica supported iron nanocatalyst have been synthesized by the modified colloidal method. The nanoparticles were synthesized at iron loadings of 3, 5 and 6 wt.% while the ratio between the precursor and the surfactant was maintained at 1:18. XPS analysis revealed the presence of Fe₃O₄ on the SiO₂ support. TPR analysis showed that the increase of Fe loadings caused the first reduction temperature of the nanocatalysts to shift to higher temperature. TEM analysis enabled profile views of the SiO₂-supported Fe nanocatalyst to be captured. The size of iron particles were in the range of 4 to 20 nm. The 6 wt.% Fe/SiO₂ showed a narrower particle size distribution than those obtained from the other two samples.
catalyst models and was chosen as the best spherical catalyst model.

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REFERENCES


