Effect of Magnesium Promoter on Nickel/Kieselguhr Catalysts in Triglyceride Oil Hydrogenation

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Abstract: The effects of a magnesium promoter on the catalytic properties of kieselguhr-supported nickel catalysts were examined through a triglyceride oil hydrogenation reaction. The catalysts were characterized with respect to their BET surface area, pore size distribution, hydrogen chemisorption, temperature-programmed reduction (TPR), and X-ray diffraction (XRD). The reactions were performed at 180°C and 45 psi. By adding a small amount of magnesium to a kieselguhr-supported nickel catalyst, the BET surface area increases as a result of an increase in microporosity. With the addition of magnesium, the catalysts were more difficult to reduce, but presented a higher metallic area. In the hydrogenation of triglyceride oil, the 4 wt% magnesium-promoted catalyst showed the highest activity, which appeared to be due to an increase of the metallic area as well as maintaining mesoporosity to avoid limited diffusion.

Keywords: nickel, magnesium, kieselguhr, triglyceride oil hydrogenation, promoter effect

Introduction

Hydrogenation of triglyceride oil is an important process in the chemical and food industries. This process has been used to produce the raw materials of such products as resin, vegetable fat, margarine, cosmetics, and soap. Vegetable oil is composed primarily of triglycerides, which are esters of glycerol and fatty acids. The most common fatty acid chains included in vegetable oil are saturated compounds, such as palmitic acid and stearic acid, and unsaturated compounds, such as oleic acid, linoleic acid, and linolenic acid.

The purpose of vegetable oil hydrogenation is to increase the stability of the oil. Highly unsaturated oil is susceptible to autoxidation, thermal decomposition, and other reactions that affect flavor [1]. Therefore, it is advantageous to partially hydrogenate the oil to improve its stability for storage and transport. However, if there is a large quantity of stearic acid or trans isomers in the vegetable oil, the oil becomes gritty, a tactile sensation due to a relative increase in the melting point. Therefore, it is necessary to convert linoleic acid to oleic acid selectively to inhibit the increase of the concentration of stearic acid or the production of trans isomers by isomerization.

While homogeneous catalysts have been investigated [2], the use of a heterogeneous catalyst has proven to be most effective in achieving the desired fatty acid composition and melting properties [3-10]. In this process, the catalyst is a solid while the reactants are in liquid and gas states. The reaction is performed as a batch slurry reaction in industrial applications. Nickel-supported catalysts are usually employed for the selective hydrogenation of triglyceride oil. Although other catalysts, including novel metals, platinum, rhodium, and palladium, have also been investigated, they are costly for industrial uses. Consequently, silica- or kieselguhr-supported nickel catalysts, prepared by precipitation or impregnation, have been used extensively in many industrial processes.

While numerous studies have been conducted with the aim of developing controlled catalyst preparations [1,11,12], there has been relatively little effort to elucidate the

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Table 1. Physical Properties of 40 wt% Nickel/Kieselguhr Catalysts

<table>
<thead>
<tr>
<th>Amount of magnesium (wt%)</th>
<th>BET surface area (m²/g)</th>
<th>Average pore diameter (Å)</th>
<th>Nickel surface area (m²/g)</th>
<th>Nickel particle diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>153</td>
<td>47</td>
<td>27</td>
<td>66</td>
</tr>
<tr>
<td>4</td>
<td>153</td>
<td>41</td>
<td>30</td>
<td>58</td>
</tr>
<tr>
<td>8</td>
<td>162</td>
<td>40</td>
<td>36</td>
<td>40</td>
</tr>
</tbody>
</table>

<sup>a</sup>Calculated by H₂ chemisorption; <sup>b</sup>Determined by XRD.

effects of promoters on the catalytic properties in triglyceride oil hydrogenation. In this paper, the effects of magnesium on the catalytic activity and selectivity of triglyceride oil hydrogenation have been investigated. The catalyst samples were characterized with respect to their BET surface area, pore size distribution, hydrogen chemisorption, temperature-programmed reduction (TPR), and X-ray diffraction (XRD).

### Experimental

**Catalysts**

Ni(NO₃)₂·6H₂O (Junsei), nickel acetate (Aldrich), and Mg(NO₃)₂·6H₂O (Yakuriri), were used as precursors, and kieselguhr (Fluka) was used as a support. Na₂CO₃ (Yakuriri) and urea (Aldrich) were used as precipitants. Hydrogen and nitrogen (Matheson, 99.999%) were further purified by using a molecular sieve trap.

Catalysts were prepared following the conventional precipitation method described by Suh and coworkers [13]. For the nickel/kieselguhr catalyst, kieselguhr, Ni(NO₃)₂·6H₂O, urea, and deionized water were introduced into a four-neck flask to make a 400-cc aqueous solution. After this solution was heated to 90°C, a precipitant solution was introduced via a metering pump. The final pH of the solution was approximately 8. After filtering and washing, the catalysts were dried overnight in air at 120°C.

**Characterization**

BET surface areas, pore volumes, and pore size distributions were measured by nitrogen adsorption-desorption at 77 K using a Micromeritics ASAP 2000 instruments. The prepared catalysts were reduced without calcinations at 450°C for 4 h in a stream of hydrogen. The nickel surface area of the reduced catalyst was estimated from the amount of hydrogen chemisorption on the catalyst. This measurement was performed using a Micromeritics ASAP 2010. The average size of the reduced nickel particles was estimated with an X-ray diffractometer (Rigaku, D/MAX-III, 3 kW) using Cu Kα radiation. The average nickel particle size was calculated using Scherrer’s equation from the width of the peak at 44.6° representing Ni(111). To avoid contact with air, XRD spectra were obtained by using the reduced catalyst impregnated in vegetable oil. Temperature-programmed reduction (TPR) measurements were performed on samples of the precursors using a Micromeritics Chemisorb 2750, equipped with a quadruple mass spectrometer, at a heating rate of 10°C/min.

**Reaction**

A commercial refined vegetable oil was used as a reactant, with the following composition of fatty acid radicals (carbon atoms:double bonds) in the triglycerides: 11.3 mol% palmitic acid (C16:0), 4.4 mol% stearic acid (C18:0), 25.2 mol% oleic acid (C18:1), 52.7 mol% linoleic acid (C18:2), and 5.3 mol% linolenic acid (C18:3). The liquid phase hydrogenation of vegetable oil was performed in a 300-mL stainless-steel autoclave equipped with a magnetic driven agitator. The reaction tests were performed under the following conditions: reaction temperature, 180°C; hydrogen pressure, 45 psi; reactant, 160 mL of vegetable oil; catalyst concentration, 0.03 wt% nickel. The reaction rate was calculated from the consumption of hydrogen in a storage reservoir whose pressure was monitored by a pressure transducer.

The reactants and the products were analyzed after esterification with methanol. Their compositions were determined by using an Agilent 6890 gas chromatograph with a Supelcowax capillary column (L, 30m; I.D., 0.25 mm; thickness of film, 0.25 μm). For the quantitative determination of trans isomers, the methyl ester obtained was dried under vacuum and then diluted with CS₂, and subsequently injected into a sealed liquid FTIR cell (thickness: 0.2 mm) having a NaCl window using a Bomem Infrared Fourier Transform Model 101 Spectrometer. IR spectra were collected in the range from 1150 to 900 cm⁻¹. The amount of trans isomer was calculated by comparison with a standard sample, methyl elaidate [14].

### Results and Discussion

**Characterization of Catalysts**

Table 1 lists the BET surface area, average pore diameter, and nickel particle size of the 40 wt% nickel/kieselguhr catalysts incorporating magnesium promoter. As the concentration of magnesium increases from 2 to 8 wt%, the BET surface area increases significantly. As the
concentration of magnesium increases, the average pore diameter decreases. Figure 1 shows the pore size distribution over the catalysts containing the promoters. While the catalysts with 2~4 wt% magnesium have numerous mesopores in the 40-Å range, the proportion of micropores for the 8 wt% magnesium-promoted catalyst is much larger than those of the other catalysts. The increase in the BET surface area upon the addition of magnesium appears to be due to the formation of micropores.

Figure 2 shows XRD spectra of the nickel/kieselguhr catalysts with and without added magnesium. The XRD spectra present peaks associated with metallic nickel, MgO, and Ni$_2$SiO$_4$ [15,16]. Kim and coworkers [17] reported that an MgNiO$_2$ phase (2 $\theta$ = 43°, 62.5°, 37°, 78.9°, 74.8°) could be formed with 13 wt% Ni/MgO catalyst.

The peaks of MgNiO$_2$ are not observed over the nickel/kieselguhr catalysts containing added magnesium in the present work. The peak representing nickel decreases in intensity upon the addition of magnesium. As shown in Table 1, the nickel particle size decreased from 94 to 40 Å upon the addition of magnesium from 0 to 8 wt%. Table 1 also shows that the surface area of the nickel metal increases upon the addition of magnesium.

The TPR curves of the catalysts are presented in Figure 3. A number of groups have investigated the reduction of supported nickel catalysts by TPR and have observed several reduction peaks centered at different maximum temperatures in the TPR profiles [18,19]. It is well known that Ni$^{2+}$ is directly reduced to metallic Ni without going through intermediate oxides. For the TPR of NiO, the reported peak maximum of reduction is around 600~700 K, which can be slightly influenced by the source of the NiO and the experimental conditions [15,20]. The peaks in Figure 3 can be attributed to the reduction of NiO particles, which can be detected by XRD analysis. High temperature peaks that can be assigned to the reduction of NiO having intimate contact with the support [15,18] are not observed in the present work.

The TPR data for the nickel/kieselguhr catalysts provide evidence that the sample is characterized by a relatively uniform phase composition of nickel. This finding could be predicted from the result that the reduction proceeds in one step (Figure 3). The addition of magnesium into the nickel/kieselguhr catalyst does not result in the formation of new compounds in the sample. The major part of hydrogen absorbed on nickel-magnesium, as well as on the unpromoted nickel/kieselguhr catalyst, corresponds to one peak. When 2.0~8.0 wt% magnesium is added into the nickel/kieselguhr catalyst, this peak is shifted from 590 to 620 K, i.e., magnesium causes an increase in the reduction temperature of the nickel oxide phases. From the observation above of a slight increase
Table 2. Effects of Magnesium Promoter on Product Distribution over 40 wt% Nickel/Kieselguhr Catalysts

<table>
<thead>
<tr>
<th>Fatty acid in product</th>
<th>No promoter</th>
<th>Mg 2 wt%</th>
<th>Mg 4 wt%</th>
<th>Mg 8 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C16:0</td>
<td>11.7</td>
<td>11.4</td>
<td>11.4</td>
<td>11.4</td>
</tr>
<tr>
<td>C18:0</td>
<td>4.6</td>
<td>5.1</td>
<td>4.9</td>
<td>5.2</td>
</tr>
<tr>
<td>C18:1</td>
<td>34.0</td>
<td>37.2</td>
<td>44.1</td>
<td>37.8</td>
</tr>
<tr>
<td>C18:2</td>
<td>44.3</td>
<td>41.4</td>
<td>35.7</td>
<td>40.8</td>
</tr>
<tr>
<td>C18:3</td>
<td>4.1</td>
<td>3.5</td>
<td>2.5</td>
<td>3.4</td>
</tr>
<tr>
<td>Trans isomer</td>
<td>8.4</td>
<td>11.6</td>
<td>15.1</td>
<td>13.4</td>
</tr>
</tbody>
</table>

Reaction conditions: 180°C, 45 psi; reaction time: 30 min; feed composition: 11.3% palmitic acid (C16:0), 4.4% stearic acid (C18:0), 25.2% oleic acid (C18:1), 52.7% linoleic acid (C18:2), and 5.3% linolenic acid (C18:3); trans isomer in feed: 2.1%.

Figure 4. Hydrogen consumption in the hydrogenation of vegetable oil over the magnesium-promoted 40 wt% nickel/kieselguhr catalysts (reaction conditions: 180°C, 45 psi).

Activity and Selectivity

Figure 4 shows the hydrogen consumption in the hydrogenation of vegetable oil over nickel/kieselguhr catalysts containing magnesium (2~8 wt%). Until a reaction time of 30 min, the magnesium-promoted catalysts show higher activity than the unpromoted catalyst. In particular, the activity of the 4 wt% magnesium-promoted catalyst is the highest among the magnesium-promoted catalysts.

This finding can be explained by the modification of the catalyst’s characteristics. Table 1 shows that the addition of magnesium results in an increase of the BET surface area and a decrease of the pore size and nickel particle size. For a smaller-pore-size catalyst, the diffusion limitation affects triglycerides having a molecule size of about 15-20 Å [11,12]. Micropores do not contribute to the progress of the reaction since the triglyceride molecules cannot reach the active sites within them. For the case of the 4 wt% magnesium-promoted catalyst, the BET surface area increases with a decrease of pore size, but the diffusion limitation effect is negligible considering that most of the pores are constituted by 40-Å mesopores. Besides the diffusion factors, the distribution and size of the nickel crystallites on the support play an important role in the activity of the reaction [1]. The increase in reaction activity can be explained by the increase of the surface area of nickel metal that is due to the decrease of nickel particle size. As the nickel particle size becomes smaller, numerous nickel atoms (where the reaction can take place) are exposed to the surface. Consequently, the reaction rate increased as a result of the increase in the number of active sites.

For the 8 wt% magnesium-promoted catalyst, the average nickel particle size is 40 Å and this catalyst mostly has micropores having sizes under 20 Å. This situation can cause a diffusion limitation. Balkos and coworkers [1] reported that micropores inhibit the participation of triglyceride in the hydrogenation reaction as a result of the limited access to active sites. The low activity of 8 wt% magnesium-promoted catalyst can be explained by this diffusion limitation despite the increase in nickel particle surface area. In addition to the diffusion limitation, the low activity of 8 wt% magnesium-promoted catalyst seems to be due to difficulty of reduction, which can be evidenced in the TPR results. TPR experiments showed that the reducibility of the nickel oxide particles decreases when the magnesium content of the samples increased. Consequently, an optimal magnesium content (4 wt%) exists for the highest activity in triglyceride hydrogenation reaction.

Table 2 shows the product distribution in triglyceride hydrogenation. Another aim of this reaction is to minimize stearic acid (C18:0) formation and reduce the contents of linolenic acid (C18:3) and linoleic acid (C18:2). It is also desirable to reduce the formation of isomers of trans fatty acids [9]. From this point of view, the 4 wt% magnesium-promoted catalyst resulted in almost no increase in the amount of stearic acid and a selective de-
crease in the amounts of linolenic acid (C18:3) and linoleic acid (C18:2). However, an increase in the amounts of trans isomers is inevitable upon increasing the reaction activity.

**Conclusion**

By adding a small amount of magnesium to a kieselguhr-supported nickel catalyst, the BET surface area increased as a result of the increase in microporosity. With the addition of magnesium, the catalysts became more difficult to reduce, but they presented a higher metallic area. In the hydrogenation of triglyceride oil the 4 wt% magnesium-promoted catalyst showed the highest activity, which appeared to be due to the increase of the metallic area as well as maintaining mesoporosity to avoid limited diffusion.

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**References**