Synthesis and Catalytic Evaluation of Mesoporous Molecular Sieve Supported Hydrocracking Catalysts

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Abstract
A series of hydrocracking catalysts based on mesoporous molecular sieves of MCM-41 and SBA-15 with different silica to alumina ratios was prepared. Nickel and molybdenum were used as active metals to impregnate the extrudates prepared by using molecular sieves. The catalysts were characterized for physical and chemical properties and evaluated for the hydrocracking of desulfurised vacuum gas oil. The conversion of DS-VGO was lower as compared to that of the catalyst based on USY zeolite. However, the gas yield was lower in case of mesoporous materials based catalysts.

Introduction
Zeolites are widely used as catalysts in petroleum refining and for the production of petrochemicals and fine chemicals. Recently, the breakthrough discovery of the M41S family mesoporous materials [1,2] exemplified by the MCM-41 bearing hexagonal-close-packed channels. Despite the excellent structural properties, the hydrothermal stability of MCM-41 and MCM-41-like mesoporous materials was reported as lower than their counter part zeolites. Recently, a new kind of mesoporous silica, SBA-15, has been synthesized with poly(alkylene oxide) triblock copolymers such as poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) (PEO-PPO-PEO) [3]. Beside its uniform and large pore size channels (4.6-30 nm), SBA-15 possesses thick walls (3.1-6.4 nm). Therefore, it has much higher hydrothermal stability than MCM-41 [3]. Owing to their extremely large surface area (generally exceeding 1000 m²g⁻¹) and ultra large pore size these mesoporous materials have attracted great practical and academic interest as acid-catalyzed reactions of large molecules such as hydroprocessing of residual oil [4-5].

In this study, the preparation of MCM-41 and SBA-15 with Si/Al 10, 20 and hydrocracking catalysts based on these mesoporous materials along with USY zeolite are presented. Commercial USY zeolite used in this study also has mesopores in it. Nickel and
molybdenum are impregnated as active metals. Mesoporous materials and hydrocracking catalysts prepared were characterized by XRD, surface area, pore volume, pore-size distribution, particle size measurement, and acidity measurement by FTIR and ammonia TPD. The side crushing strength of the extrudates with alumina binder was also measured by crushing strength tester. The catalysts were evaluated for hydrocracking of desulfurized vacuum gas oil (DS-VGO). The hydrocracking activity was measured by GC-SIMDIST method and sulfur and nitrogen contents of the product were measured by elemental analyzer.

Experimental

Synthesis of Mesoporous Molecular Sieves.

Synthesis of Al-MCM-41 was followed by the procedure described by Kim and co-workers [6]. Two samples were prepared with Si/Al ratio of 10 and 20. A pure silica SBA-15 has been synthesized following a procedure of Stuky and co-workers [5] with some variations adopted by Cheng et.al., [7]. Al-SBA-15 was obtained by treating pure silica sample with predetermined amount of aluminum isoperoxide in a solution of n-hexane to get Si/Al ratios of 10 and 20. The Al-MCM-41 and Al-SBA-15 samples were calcined in air at 500 °C for 5 h and then ion-exchanged with 0.1 M solution of HNO$_3$ for 3-4 days, changing fresh HNO$_3$ solution twice every day. Final calcination of the ion-exchanged sample was carried out in air at 500 °C for 5 h to obtain H-type of Al-MCM-41 and Al-SBA-15.

Catalyst Preparation.

Extrudates of 50% zeolitic materials and alumina binder (Cataloid AP-1, supplied by CCIC of Japan) were prepared in 1/32 inch of diameter. USY zeolite HSZ-330 HOA was supplied by Tosoh Company, Japan. The typical preparation procedure was as follows: 7.00 g of zeolite was mixed with 9.86 g of alumina binder (71% Al$_2$O$_3$) in a Teflon beaker with stainless steel spatula. After through mixing of the two solid 14.0 g of distilled water was added drop wise with constant mixing. After kneading the mixture was loaded into a steel syringe (20 ml) with a 1/32” dice and extrudates were obtained with the help of oil jack. The amount of water varied for various mesoporous materials. The extrudates prepared were dried in oven at 120 °C for 2 hours and calcined in dry flowing air for 2 hours at 550 °C in a quartz tube in horizontal muffle furnace. The calcined extrudates were stored in screw capped glass bottles.
Hexaammonium hepatmolybdate tetrahydrate (99.05, Kanto Chemical Co., Japan) and nickel nitrate hexahydrate (98.0%, Junsei Chemical Co., Japan) were used as sources for molybdenum and nickel, for loading on to the extrudates, respectively. Incipient wetness method was used for the impregnation of metals on the extrudates. Molybdenum was impregnated first followed by nickel impregnation. In between two successive impregnations the catalyst samples were dried and calcined up to 550 °C for 2 hours. Finally the catalyst samples were dried in flowing air and calcined at 550 °C for 2 hours.

Characterization Methods.
The BET surface area and pore volume of all the catalysts were measured by an Autosorb-1 gas sorption analyzer (Quantachrome Corporation, USA) using nitrogen at 77 K. The particle size measurement was performed by Photal DLS-6000 HL instrument, supplied by Otsuka Electronics of Japan. A 10 mg sample of mesoporous molecular sieve was dispersed in 10 ml of distilled water. The sample was treated in an ultrasonic bath for five minutes for better dispersion. The measurement results are reported as a particle size diameter of number averaged distribution. The acid properties of hydrocracking catalysts were determined by temperature-programmed desorption of ammonia. The system was supplied by Bell Japan Inc. (Model TPD-1-A). FTIR analyses of pyridine adsorbed mesoporous molecular sieves were performed for the acidity measurement. This technique is utilized for the measurement of Brönsted and Lewis acid sites selectively. Powder X-ray diffraction patterns of mesoporous molecular sieves were recorded on a Rigaku RINT 2400 diffractometer using Cu Kα radiation.

Catalyst Evaluation.
Hydrocracking activity of four catalyst samples was measured in fixed bed micro flow reactor under mild hydrocracking conditions. Desulfurized vacuum gas oil (DS-VGO) feed was used for the hydrocracking reaction. Properties of feedstock and reaction condition are summarized as follows:

*Feedstock: DS-VGO*

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density 15°C</td>
<td>0.8819 g/cm³</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.017 wt%</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.01 wt%</td>
</tr>
</tbody>
</table>
**Reaction condition:**

Temperature 370 °C  
Pressure 80 kg/cm²  
LHSV 1.0 h⁻¹  
Hydrogen flux 10NL/h  
\( \text{H}_2/\text{Oil} \) 1000 L/L  
Reaction Time 7 h

In a typical run, 10 cc of the catalysts extrudates (1/32 in) were loaded in a stainless steel tube reactor (capacity 10 cc) placed in a sand bath. All the catalysts were sulfided in a flow of 5% \( \text{H}_2\text{S} \) for two hours at 400 °C. Then the reactor was cooled to the reaction temperature i.e., 370 °C. The feed was introduced at a rate of 10 cc/h and the product sample was collected after seven hours. The product tank was purged twice before collecting a two hour sample of gas and liquid separately. The liquid product was analyzed by simulated gas chromatography to calculate the conversion of DS-VGO. The conversion was calculated as weight fraction < 343 °C.

**Results and Discussion**

The results of surface area, pore volume, pore size, and particle size, and TPD of ammonia of mesoporous materials are summarized in the following Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S.A (m²/g)</th>
<th>P.V (cc/g)</th>
<th>Pore Dia. (Å)</th>
<th>Particle Size (µm)</th>
<th>Acidity (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCM-41(10)</td>
<td>781</td>
<td>0.864</td>
<td>24.4</td>
<td>1.82 ±0.18</td>
<td>0.34</td>
</tr>
<tr>
<td>MCM-41(20)</td>
<td>990</td>
<td>0.884</td>
<td>27.2</td>
<td>1.40 ±0.22</td>
<td>0.25</td>
</tr>
<tr>
<td>SBA-15 (10)</td>
<td>555</td>
<td>0.823</td>
<td>77.1</td>
<td>1.73 ±0.12</td>
<td>0.36</td>
</tr>
<tr>
<td>SBA-15 (20)</td>
<td>636</td>
<td>0.890</td>
<td>77.7</td>
<td>1.50 ±0.13</td>
<td>0.25</td>
</tr>
<tr>
<td>USY-Zeolite</td>
<td>609</td>
<td>0.365</td>
<td>10.5</td>
<td>-</td>
<td>1.37</td>
</tr>
</tbody>
</table>

a. Value in the parenthesis is Si/Al ratio  
b. BJH Method Adsorption Pore Diameter  
c. Average particle size of SBA-15 as-synthesized form = 1.60 ±0.11

The above results show that all the samples have high surface area however the highest is for MCM-41 (20), on the other hand minimum value is for SBA-15 (10). These results also show that for same type of material, the sample with high silica to alumina ratio exhibits higher surface area as compared with the samples with lower silica to alumina ratios. This could be attributed to the lower crystallinity observed by the XRD results. Similarly, pore volume of
these materials is very large as compared with USY zeolite. Large pore volume and pore diameter is required for heavy oil applications. The results of acidity measurement show that the amount of acidity depends upon the Si/Al ratio of mesoporous molecular sieves regardless of the type of material. However, the amount of acidity is fairly low for mesoporous molecular sieve as compared with that of commercial USY zeolite. Figure 1 shows the XRD pattern of SBA-15 samples. The unit cell size for SBA-15 types of materials are quite larger as compared with MCM-41 type (40.1 Å for Si/Al 10 and 43.3 for Si/Al 20) molecular sieves.

![Figure 1](image)

Physical and catalytic properties of selected prepared hydrocracking catalysts are given in Table 2. Initial hydrocracking activity of four catalyst samples was measured in a fixed bed micro flow reactor (10 cm³ catalyst volume) at 370 °C and 80 kg/cm² for seven hours at a liquid hourly space velocity of 1.0 h⁻¹. Desulfurized vacuum gas oil (DS-VGO) feed was used for the hydrocracking reaction. The results of hydrocracking activity indicate that a lower gas yield was obtained with mesoporous molecular sieve based catalysts as
compared with USY zeolite base catalyst. However, highest cracking activity was observed with USY based catalyst. This is due to very high acidity of USY zeolite as compared with other materials used in this study. The liquid yield was very low (40%) in case of Catalyst-D as compared with (above 95%) other catalysts. The overall results show that mesoporous molecular sieves have potential to be used as hydrocracking catalysts.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Support *</th>
<th>S.A (m²/g)</th>
<th>Pore Vol. (cc/g)</th>
<th>Bulk density (g/cc)</th>
<th>DS-VGO Con. (%)</th>
<th>Gas yield (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat-A</td>
<td>MCM-41 (10)</td>
<td>340</td>
<td>0.353</td>
<td>0.604</td>
<td>54.0</td>
<td>4.43</td>
</tr>
<tr>
<td>Cat-B</td>
<td>SBA-15 (10)</td>
<td>253</td>
<td>0.416</td>
<td>0.526</td>
<td>21.2</td>
<td>1.33</td>
</tr>
<tr>
<td>Cat-C</td>
<td>SBA-15 (20)</td>
<td>298</td>
<td>0.464</td>
<td>0.555</td>
<td>19.8</td>
<td>1.59</td>
</tr>
<tr>
<td>Cat-D</td>
<td>USY-zeolite</td>
<td>292</td>
<td>0.290</td>
<td>0.694</td>
<td>92.2</td>
<td>15.6</td>
</tr>
</tbody>
</table>

*50% mixture of H-form of Al-zeolitic material and alumina binder, impregnated with 10% MoO₃ and 4% NiO.

**Conclusions**

Mesoporous molecular sieves of MCM41 and SBA-15 type have been synthesized successfully with Si/Al ratios of 10 and 20. The results of characterization of these material reveals the structure and other properties are of typical mesoporous material. Catalyst based on USY zeolite showed highest hydrocracking activity. MCM-41(10) based catalyst also showed good catalytic activity. On the other hand catalysts based on SBA-15 showed lower activity. However gas yield was higher and liquid yield was very low for USY zeolite based catalyst as compared with MCM-41 based catalyst.

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**References**


