

# Mesoporous Zeolite-Supported Noble Metal Catalysts for Low-Temperature Hydrogenation of Aromatics in Distillate Fuels

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## Introduction

The present work is concerned with deep hydrogenation of aromatics in distillate fuels at low temperatures using mesoporous zeolite-supported noble metal catalysts. This work is a part of our on-going effort to develop advanced thermally stable jet fuels from coal-derived liquids and petroleum. Saturation of naphthalene and its derivatives not only reduces aromatics contents of jet fuels, but also generates decalins which show much higher thermal stability than long-chain alkanes in jet fuels at high temperature (Song et al., 1994). This work also has a bearing on developing new catalytic processes for low-temperature hydrogenation of distillate fuels.

The Clean Air Act Amendments of 1990 and new regulations call for the production and use of more environmentally friendly transportation fuels with lower contents of sulfur and aromatics (Lee et al., 1993; Unzelman, 1993). High aromatic content in distillate fuels lowers the fuel quality and contributes significantly to the formation of environmentally harmful emissions (Stanislaus and Cooper, 1994). California Air Resources Board (CARB) has passed legislative measures to limit the sulfur and aromatic contents of diesel fuel to 0.05 wt% and 10 vol%, respectively, effective October 1993 (Lee et al., 1993). Currently, conventional hydrotreating technology is adapted for aromatics saturation. Some studies have shown that complete hydrogenation of aromatics is not possible owing to equilibrium limitations under typical hydrotreating conditions, and existing middle distillate hydrotreaters designed to reduce sulfur and nitrogen levels would lower the diesel aromatics only marginally (Stanislaus and Cooper, 1994).

Deep hydrogenation may become necessary in the near future for reducing aromatic contents of distillate fuels to meet increasingly more stringent regulations. One of the significant findings by The US Auto/Oil Air Quality Improvement Research Program (which involved Ford, General Motors, Chrysler, and 14 largest US petroleum companies) is that lowering aromatic content lowers toxic emissions (Kreucher, 1995; Unzelman, 1993). The significant findings of the European Program on Emissions, Fuels, and Engine Technologies (EPEFE) also include the following related to aromatics: 1) decreasing aromatics reduces catalytic converter light-off time, improves the converter efficiency and decreases exhaust hydrocarbons; and 2) decreasing fuel polyaromatics reduces light-duty diesel exhaust nitrogen oxides and particulate material and heavy-duty exhaust hydrocarbons, nitrogen oxides, and particulate material (Kreucher, 1995).

Typical conventional catalysts for fuel hydroprocessing are sulfided Co-Mo and Ni-Mo supported on alumina. However, such catalysts are active only at relatively high temperatures (e.g., >300°C). Because hydrogenation is exothermic, deep hydrogenation is favored at lower temperature. It is therefore natural to consider deep hydrogenation at low temperatures (e.g., ≤300°C), and the potential candidate catalysts for low-temperature hydrotreating include noble metals. Since it is known that noble metal catalysts are easily deactivated by sulfur compounds, a two-stage processing strategy may be adopted. The first stage would involve deep desulfurization of the fuels using metal sulfide catalysts, and the second stage deals with deep hydrogenation over noble metal catalysts. Such a two-stage processing scheme may become practically applicable, since deep desulfurization is likely to be required by regulations to further reduce sulfur contents of transportation fuels in the near future.

The objective of this work is to explore the potential of mesoporous zeolite as support of noble metal catalysts for deep hydrogenation of aromatics in jet fuel and diesel fuel. Recently, Mobil researchers have invented MCM-41 type mesoporous molecular sieves possessing a hexagonal array of uniform mesopores (Beck et al., 1992; Kresge et al., 1993). We have synthesized mesoporous zeolites with MCM-41 type structure using three different aluminum sources (Reddy and Song, 1996a, 1996b). We are currently exploring their applications for catalytic fuel processing (Reddy and Song, 1996b; Song and Reddy, 1996). In our preliminary work, Pt/MCM-41 catalysts containing 3 wt% Pt were prepared with the mesoporous zeolites synthesized using pseudo boehmite, Al isopropoxide, and Al sulfate, and applied for hydrogenation of naphthalene at 200°C and that of phenanthrene at 300°C. The results showed that the sample made by using Al isopropoxide gives the best catalyst (Reddy and Song, 1996b). In the present work, supported catalysts containing 2 wt% Pt or 2 wt% Pd were prepared using proton-form MCM-41

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(synthesized using Al isopropoxide) as well as  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  as the support materials. This paper reports on their performance for hydrogenation of naphthalene in n-tridecane at 200°C.

## Experimental

### Catalyst Preparation

The mesoporous zeolite with MCM-41 type structure was synthesized using aluminum isopropoxide as the Al source according to the procedure described elsewhere (Reddy and Song, 1996). Supported catalysts containing 2 wt% Pt or 2 wt% Pd were prepared using proton-form mesoporous MCM-41 zeolite as well as  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  as the support materials. Table 1 gives their properties. The Pt catalysts were prepared by impregnation from aqueous solution of hydrogen hexachloro platinate (IV) hydrate,  $\text{H}_2\text{PtCl}_6 \cdot \text{xH}_2\text{O}$  (Aldrich, 99.995% Pt, metal basis). The Pd catalysts were prepared by impregnation of  $\text{PdCl}_2$  (Aldrich, 99.999% Pd, metal basis) dissolved in dilute hydrochloric acid (sufficient to form soluble  $\text{PdCl}_4^{2-}$ ). In both cases, water was removed by rotary evaporation at about 60°C. The catalyst precursors were dried in an oven at 60°C overnight, and then calcined in an electric furnace at 450°C for 4 h. The nominal metal concentration was kept at 2 wt% for both Pt and Pd catalysts. Metal reduction was done in situ during naphthalene hydrogenation tests.

### Catalyst Evaluation

All the catalysts were tested at 200 °C for a given residence time in 25-mL stainless-steel microautoclaves. The total volume of the system including the connecting tube between reactor and pressure gauge is about 30 mL. Typically, the reactor was charged with 1.0 g naphthalene (Aldrich, 99%), 4.0 g n-tridecane solvent, and 0.1 g catalyst. The charged reactor was flushed with  $\text{H}_2$ , then pressurized to 1000 psig (cold) to start the test. The reactor was mounted on a holder, immersed in a fluidized sand bath preheated to 200°C, and shaken vertically at 240 cycles/min with a 1 cm stroke.

At the end of the test, the reactor was taken out of the sandbath, quenched in cold water, and then allowed to cool down in air to room temperature. The gaseous products were collected for analysis and then the reactor was opened. The contents of the reactor were washed with acetone onto a filter. Solution products were analyzed by GC-MS and GC-FID. The capillary columns were 30m $\times$ 0.25mm DB-5 (J&W Scientific) for GC-MS and 30m $\times$ 0.25mm DB-5 (Hewlett-Packard), for GC-FID and the oven temperature program for both GC instruments was 60-280 °C at 10 °C/min. GC and GC-MS indicate that cracking or isomerization of n-tridecane, if any, were negligible. The yields of products were determined by quantitative GC analysis using n-nonane as internal standard, and the conversion was determined by the amount of naphthalene recovered after the reaction.

Selected tests were conducted to examine the effect of pre-reduction. Pre-reduction was carried out at 200°C for 1 h under reaction conditions except that naphthalene was not present during the reduction stage. After the reduction, the reactor was cooled down to ambient temperature, vented and opened. The reactor was re-sealed after the addition of 1 g naphthalene, and re-pressurized to 1000 psig  $\text{H}_2$  at room temperature. Hydrogenation over the pre-reduced catalysts was also conducted at 200°C for 0.5 h.

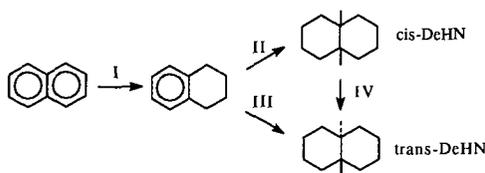
**Table 1.** Properties of the Mesoporous MCM-41 Zeolite, Titania and Alumina Supports

Support ID	Material Type	Surface Area, m <sup>2</sup> /g	Pore Vol cc/g	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> mol ratio	Source
MCM-41	Mesoporous zeolite	1206	1.77	40.7	PSU Fuel Science, Synthesized with Al
TiO <sub>2</sub>	Titania	53	---	---	Degussa, Titania P25
Al <sub>2</sub> O <sub>3</sub>	$\gamma$ -Alumina	113	---	<0.001	Degussa, Aluminum Oxide C

## Results and Discussion

Table 2 shows the distribution of products from naphthalene hydrogenation over Pd and Pt catalysts at 200°C for 60 min. The main products from naphthalene hydrogenation were tetrahydronaphthalene (tetralin or THN), and cis- and trans-decahydronaphthalene (decalin or DeHN).  $\Delta$ 9,10-octalin was also detected as a minor product in many tests, which is an intermediate from tetralin to decalin. The selectivity to tetralin+decalin+octalin approaches to unity in all the runs, indicating that there were essentially no side reactions such as ring-opening cracking

and ring-contraction isomerization under the conditions. Based on the present and previous results (Lai and Song, 1996; Schmitz et al., 1996), the reaction pathways can be represented by Scheme I.



Scheme I

### Effect of Supports

For Pt catalysts on different supports, the yield of tetralin decreased in the order of alumina > titania > MCM-41, whereas the yields of trans- and cis-decalins increased in the order of alumina < titania < MCM-41. In the case of Pt/MCM-41, the intermediate product tetralin was almost completely hydrogenated, whereas tetralin still remains as a major product with Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/TiO<sub>2</sub>.

**Table 2** Hydrogenation of Naphthalene at 200°C for 60 min over Pt and Pd Catalysts

Expt ID	79	115	81	82	83	84
Catalyst	Pt/Al <sub>2</sub> O <sub>3</sub>	Pt/TiO <sub>2</sub>	Pt/MCM-41	Pd/Al <sub>2</sub> O <sub>3</sub>	Pd/TiO <sub>2</sub>	Pd/MCM-41
<b>Conversion (%)</b>	98.3	99.9	100.0	99.9	99.9	100.0
<b>Selectivity (wt%)</b>						
Tetralin	57.0	35.8	0.0	42.5	30.5	0.0
9,10-Octalin	0.8	1.0	0.0	0.7	0.3	0.0
trans-Decalin	10.6	14.9	50.2	34.6	43.9	64.4
cis-Decalin	31.1	47.9	49.4	22.0	25.1	35.4
Others	0.5	0.4	0.4	0.2	0.2	0.2
<b>trans-/cis-DeHN</b>	0.3	0.3	1.0	1.6	1.7	1.8
<b>DeHN+Tetralin</b>	98.7	98.6	99.6	99.1	99.5	99.8
<b>DeHN/Tetralin</b>	0.7	1.7	2444.3	1.3	2.3	1235.3

For Pd catalysts, we observed essentially the same trends in terms of catalytic activity reflected by the increasing yields of decalins or decreasing yields of tetralin. Moreover, both Pd/MCM-41 and Pt/MCM-41 catalysts promoted the hydrogenation to completion such that the dominant products are trans- and cis-decalin, whereas tetralin is still one of the major products with both Al<sub>2</sub>O<sub>3</sub>- and TiO<sub>2</sub>-supported Pd and Pt catalysts. These results indicate MCM-41 supported Pt and Pd catalysts are more active than titania and alumina supported catalysts.

The higher activity of the mesoporous zeolite-supported Pt and Pd may be due to better dispersion of the noble metals on MCM-41, since it has much larger surface than that of Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> supports (Table 1). According to a recent report (Koussathana et al., 1991), hydrogenation of naphthalene and benzene is insensitive to the geometric structure of the Pt species. The mild acidity of MCM-41 may also be a contributing factor, since it contributes to the electron deficiency of the metal on zeolite surface. It is known that noble metals on Y-zeolite and mordenite are often better dispersed and electron deficient as compared to those on alumina (Stanislaus and Cooper, 1994). The zeolitic protons can act as chemical anchors for reduced noble metal particles (Satchler and Zhang, 1993).

The selectivity to decalin isomers depends on the support and metal type. Compared to Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/TiO<sub>2</sub> catalysts, Pd/MCM-41 catalyst afforded higher trans/cis ratio, indicating a higher selectivity to trans-decalin. There appears to be one major difference between Pt and Pd catalysts in selectivity: Pd shows higher selectivity to trans-decalin. Therefore, among the three supports, MCM-41 corresponds to higher trans/cis ratios. Among the two metals, Pd catalysts always afford higher trans/cis ratios. Overall, MCM-41 supported Pd catalyst display highest selectivity to trans-decalin.

### Effect of Reaction Time

Since complete naphthalene conversion was reached in 1 h, we reduced the residence time and conducted 30 min runs at 200°C. Table 3 shows the results. Although unreduced catalysts were used, nearly complete naphthalene conversion was achieved in all the runs within 30 min. However, the product distribution changed with residence time. Yields of tetralin increased and decalin yields decreased with decreasing residence time. It is also clear that the absolute yields of tetralin and decalins strongly depended on the type of support and metal.

Even with reduced residence time, the MCM-41 supported Pt and Pd catalysts are substantially more active than the corresponding catalysts supported on alumina and titania (Table 3). In general, the activity of both Pt and Pd catalysts for complete hydrogenation of naphthalene to decalin decreased in the following order with respect to the support type: MCM-41 > TiO<sub>2</sub> > Al<sub>2</sub>O<sub>3</sub>.

**Table 3** Hydrogenation of Naphthalene at 200°C for 30 min over Pt and Pd Catalysts

Expt ID	109r	110	92	93	94	111r
Catalyst	Pt/Al <sub>2</sub> O <sub>3</sub>	Pt/TiO <sub>2</sub>	Pt/MCM-41	Pd/Al <sub>2</sub> O <sub>3</sub>	Pd/TiO <sub>2</sub>	Pd/MCM-41
<b>Conversion (%)</b>	97.2	99.9	100.0	99.9	100.0	99.9
<b>Selectivity (wt%)</b>						
Tetralin	68.9	51.9	0.1	81.3	62.6	17.1
9,10-Octalin	1.1	0.2	0.00	0.9	1.0	0.3
trans-Decalin	6.5	8.2	45.2	10.3	21.1	52.8
cis-Decalin	23.3	39.0	54.3	7.4	15.1	29.7
Others	0.2	0.7	0.6	0.1	0.2	0.1
<b>trans-/cis-DeHN</b>	0.3	0.2	0.8	1.4	1.4	1.8
<b>DeHN+Tetralin</b>	98.7	99.1	99.4	99.0	98.8	99.6
<b>DeHN/Tetralin</b>	0.4	0.9	2160.2	0.2	0.6	4.8

When compared to the 60 min-runs, the yields of tetralin were generally higher and decalin yields lower in 30 min-runs, particularly when Pt or Pd was supported on alumina or titania. The trans/cis ratios of the decalin isomers are lower in the 30 min runs than in 60 min runs, even in the case of Pt/MCM-41 where tetralin was completely converted to decalin within 30 min. These results are consistent with Scheme I and indicate that cis-decalin isomerizes into trans-decalin during the hydrogenation reaction over MCM-41 supported catalysts, being consistent with the previous results from this laboratory (Lai and Song, 1996; Schmitz et al., 1996). TPD of n-butylamine indicates that hydrogen MCM-41 is acidic, but its acidity is lower than that of hydrogen Y zeolite. It appears from comparative examination that the presence of Pd metal and acid sites facilitates both tetralin hydrogenation and cis-decalin isomerization into trans-decalin.

### Effect of Pre-Reduction

The above results clearly indicate that both Pd and Pt catalysts supported on the mesoporous MCM-41 are superior over those supported on Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. It should be noted that there may be two contributing factors, since the calcined catalysts were applied without reduction pretreatment. First, the in situ generation of active metal particles by H<sub>2</sub> reduction may be slower in Al<sub>2</sub>O<sub>3</sub>- and TiO<sub>2</sub>-supported Pt and Pd than in MCM-41 supported metals. Second, the reduced metal species on MCM-41 are more active than those on Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. To see if this is the case, we examined the effect of pre-reduction under reaction conditions (hydrogenation over the pre-reduced catalysts at 200°C for 0.5 h).

The results showed that even after pre-reduction, the MCM-41 supported Pt and Pd catalysts are considerably more active than the corresponding Al<sub>2</sub>O<sub>3</sub>- and TiO<sub>2</sub>-supported Pt and Pd catalysts. The differences between the MCM-41 supported catalysts are that pre-reduced Pd/MCM-41 displayed higher activity for tetralin hydrogenation than pre-reduced Pt/MCM-41, whereas the in-situ reduced Pd/MCM-41 was less active than the in-situ reduced Pt/MCM-41. Our previous results of XRD suggested that the zeolite-supported Pt and Pd catalysts were completely reduced after 60 min or 30 min under comparable conditions (Reddy and Song, 1996; Schmitz et al., 1996). Therefore, it is considered that essentially all the noble metal species would have been reduced to metallic particles by a pre-reduction treatment at 200°C for 60 min under an initial H<sub>2</sub> pressure of 1000 psig using n-tridecane solvent. Another puzzling observation was that the pre-reduced catalysts are not always as active as the in-situ reduced catalysts under the reaction conditions employed in this work. Further study is in progress.

## Conclusions

Mesoporous MCM-41 zeolite that was synthesized by a proper method may be used as a very effective support for noble metal catalysts. For hydrogenation of naphthalene in n-tridecane at 200°C, both the Pt and Pd catalysts supported on MCM-41 zeolite are substantially more active than the corresponding catalysts supported on  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ . In general, the activity of both Pt and Pd catalysts for complete hydrogenation of naphthalene to decalin decreased in the following order with respect to the support type:  $\text{MCM-41} > \text{TiO}_2 > \text{Al}_2\text{O}_3$ .

Both Pd/MCM-41 and Pt/MCM-41 catalysts promoted the hydrogenation to completion such that the dominant products are trans- and cis-decalin, whereas tetralin is still one of the major products with both  $\text{Al}_2\text{O}_3$ - and  $\text{TiO}_2$ -supported Pd and Pt catalysts. In general, Pd catalysts showed higher selectivity to trans-DeHN, whereas higher selectivity to cis-DeHN was displayed by Pt catalysts.

The selectivity to decalin isomers also depends on the support and metal type. Among the three supports, MCM-41 gives higher trans/cis ratio. Among the two metals, Pd affords higher trans/cis ratio. In other words, Pd catalysts showed higher selectivity to trans-decalin, whereas higher selectivity to cis-decalin was displayed by Pt catalysts.

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