Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 93–95 (2004) 457–465

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Comparison of hydrogenation and mild hydrocracking activities of Pt-supported catalysts

Hong Yang [a,*], Craig Fairbridge [a], Josephine Hill [b], Zbigniew Ring [a]

[a] The National Centre for Upgrading Technology, 1 Oil Patch Drive, Devon, AB, Canada T9G 1A8
[b] Department of Chemical and Petroleum Engineering, University of Calgary, Calgary, AB, Canada T2N 1N4

Abstract

Six Pt-supported catalysts based on mordenite, pillared clay, delaminated clay and Al-MCM41 were tested for hydrogenation and mild hydrocracking activities in processing a middle distillate derived from Canadian oil sands. Experiments were performed in a fixed-bed microreactor between 260 and 380 °C, at a total pressure of 10.3 MPa and a LHSV of 1.0 h^{-1}. The results showed that, except for the untreated mordenite based catalyst, the other catalysts all had suitable pore structures to accommodate molecules as large as three-ring cycloparaffins and to convert them into smaller molecules. Dealumination made mordenite a better mild hydrocracking catalyst due to the creation of mesopores and macropores, and the reduction of surface acidity. At 320 °C, pillared clay based catalysts had the highest hydrogenation activity followed by Al-MCM41, delaminated clay and mordenite based catalysts. Delaminated clay based catalyst, despite producing the highest diesel yield at the same conversion of 343 $°C^+$ fraction, required the highest reaction temperatures. Thus, Pt/pillared clay and Pt/Al-MCM41 were the best overall catalysts, producing high aromatic conversion, high diesel yield and relatively low reaction temperature to reach 30% conversion of 343 $°C^+$ fraction.

Keywords: Hydrogenation; Hydrocracking; Catalysts

---

1. Introduction

Middle distillates derived from Canadian oil sands contain high concentrations of aromatics, often exhibit poor diesel ignition quality. To produce a high quality diesel blend stock, a process that not only can convert the aromatics in the distillate to naphthenic compounds by hydrogenation, but also can selectively open the rings of the naphthenic compounds by mild hydrocracking is required [1]. Mild hydrocracking has advantages over conventional gas oil hydrocracking in minimizing the production of undesirable light hydrocarbon gases and reducing hydrogen consumption. It was reported that in a mild hydrocracking process, with a conversion of 343 $°C^+$ fraction around 30%, an acceptable level of naphtha formation might be less than 20 wt.% [2,3]. Aromatic hydrogenation and ring opening of naphthenic compounds require bifunctional catalysts, with a noble metal hydrogenation function and an acidic cracking function. The catalysts also have to provide mesopores and macropores to accommodate the large molecules contained in these distillates [4]. Our objective is then to develop catalysts that could maximize aromatic conversion, diesel yield while minimize naphtha yield and the reaction temperature required for converting 343 $°C^+$ fraction. To meet these criteria, four types of catalyst materials based on mordenite, pillared clay, delaminated clay and Al-MCM41 have been developed at The National Centre for Upgrading Technology (NCUT). The hydrogenation and mild hydrocracking activities of the developed catalysts were tested using a hydrotreated light gas oil from an ebullated bed hydrocracker (Syncrude Canada Ltd., Fort McMurray, AB, Canada), and some of the results for each catalyst were published recently [5–7]. This paper summarizes and compares the performance of six Pt-supported catalysts based on the developed catalyst materials.

2. Experimental

Six Pt-loaded catalysts were developed in this work. Three catalysts were based on mordenite support: (1) original mordenite (Mor); (2) acid treated mordenite using 8 M HNO_3 at 95 °C for 6 h (Mor(A)); (3) steam and acid treated

---

[*] Corresponding author. Tel.: +1 780 987 8725; fax: +1 780 987 5349.
E-mail address: hyang@nrcan.gc.ca (H. Yang).

0920-5861/$ – see front matter. Crown Copyright © 2004 Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2004.06.075

mordenite (Mor(SA)). The steam treatment was operated at 606 °C for 4 h with a H_2O/N_2 volume ratio of 95/5. After the steam treatment, the mordenite was subjected to the same acid extraction conditions as was used for the second catalyst. Two catalysts were made from clay supports, one from pillared montmorillonite (PILC) and other from delaminated synthetic hectorite (DILC). Detailed catalyst preparation procedures for mordenite and clay based catalysts can be found in references [5] and [6], respectively. The last catalyst was an Al-MCM41 type mesoporous material prepared according to a patented procedure using aluminum sulfate hydrate and sodium silicate solution (27% SiO_2) as alumina and silica sources, and cetyltrimethylammonium bromide (CTABr) as template [8]. In a typical preparation, a solution made of 5.2 g aluminum sulfate, 208 g water and 35.8 g cetyltrimethylammonium bromide, was added to a second solution containing 56.6 g sodium silicate, 80 g water with 2.4 g sulfuric acid. The mixture was stirred for 30 min and placed in a sealed glass bottle at room temperature overnight. The solid product obtained was washed with deionized water, dried and calcined at 540 °C under N_2/air for 5 h to remove the template. The product was then reacted at 70 °C with ammonium nitrate solution for 4 h. The ion-exchanged product was washed and centrifuged to remove all traces of ammonium ion before being heated at 120 °C for 1 h and 505 °C for 4 h, under air.

Platinum was loaded into the catalyst supports through an ion-exchange procedure using $Pt(NH_3)_4Cl_2$ aqueous solution with a target Pt content of 1 wt.%. Catalyst extrudates (0.8 mm) were made by mixing the Pt-loaded catalyst precursors with pseudo-böehmite. The percent of pseudo-böehmite was 80 wt.% for catalysts based on mordenite and Al-MCM41, and 30% for clay based catalysts. The extrudates were named Pt/Mor, Pt/Mor(A), Pt/Mor(S+A) for the original mordenite, acid treated mordenite, steam and acid treated mordenite based catalysts, respectively; Pt/PILC for pillared montmorillonite based catalyst; Pt/DILC for delaminated synthetic hectorite based catalyst and Pt/MM for Al-MCM41 based catalyst. The extrudates were calcined at 400 °C for 4 h before use. A Micromeritics ASAP 2010 unit was used to determine the pore volume, specific surface area and pore size distributions of the catalyst supports by N_2 adsorption/desorption isotherm. The amount of acid sites of the catalyst supports were determined using ammonia temperature programmed desorption (NH_3-TPD). Inductively coupled plasma mass spectrometry (ICP-MS) was used to measure the Si, Al and Pt contents of the Pt-loaded catalyst precursors.

The hydrogenation and mild hydrocracking activities were tested in a tubular microreactor operated in the continuous up-flow mode (30.5 cm × 0.635 cm). The feedstock was obtained by hydrotreatment of the 250 °C$^+$ fraction of a light gas oil from an ebullated bed hydrocracker over a commercial NiMo/alumina catalyst to reduce sulfur and nitrogen contents to protect the noble metal catalysts. The catalyst was reduced in situ in hydrogen flow at 400 °C. Reactions were conducted at 10.3 MPa, 1.0 h^{-1} LHSV, from 240 to 380 °C and with a hydrogen gas rate of 600 NL/L feed. High total liquid yield (>99%) was obtained for all the experiments, this allowed the use of the following simplified equations to measure the catalyst hydrogenation activity (Eq. (1)), the mild hydrocracking activity (Eq. (2)) and conversion of ring compounds (Eq. (3)):

$$\text{aromatics conversion (\%)} = \frac{\text{aromatics in the feed} - \text{aromatics in the product}}{\text{aromatics in the feed}} \tag{1}$$

$$\text{mild hydrocracking activity (\%)} = \frac{343\,^{\circ}\text{C}^{+}\text{ in the feed} - 343\,^{\circ}\text{C}^{+}\text{ in the product}}{343\,^{\circ}\text{C}^{+}\text{ in the feed}} \tag{2}$$

$$\text{conversion of ring compounds (\%)} = \frac{\text{ring compounds in the feed} - \text{ring compounds in the product}}{\text{ring compounds in the feed}} \tag{3}$$

The total ring compounds consists of monocycloparaffins, dicycloparaffins, tricycloparaffins and aromatics.

The chemical compositions included four saturated hydrocarbon groups (paraffins, monocycloparaffins, dicycloparaffins and tricycloparaffins) and three aromatic groups (monoaromatics, diaromatics and triaromatics) were effectively identified by the GC-MS method [9,10]. The boiling range as well as the yields of naphtha (IBP—177 °C), diesel (177–343 °C) and 343 °C$^+$ fractions of the feed and total liquid products were estimated by ASTM D2887 simulated distillation method. The cetane number of the total liquid products was derived by the ignition quality tester (IQT^{TM}) [11]. Detailed descriptions of the characterization methods, catalyst testing procedures as well as analytical methods can be found elsewhere [5–7].

3. Results

3.1. Catalyst characterizations

Two dealuminated mordenite supports were obtained by acid treatment and the combination of steam and acid treatment. Fig. 1 presents the effect of dealumination on the pore size distribution determined by the BJH N_2 desorption method. The results show that more mesopores were obtained over dealuminated mordenite. Acid extraction created mesopores with diameters in the range of 20–80 Å. Steam treatment followed by acid extraction produced mesopores with diameters between 55 and 115 Å. The presence of these mesopores can facilitate the diffusion of larger molecules, encountered in oil sands derived distillates, to the active sites of the catalyst. The pore volume, specific surface area, average pore size and the total ammonia adsorbed by the

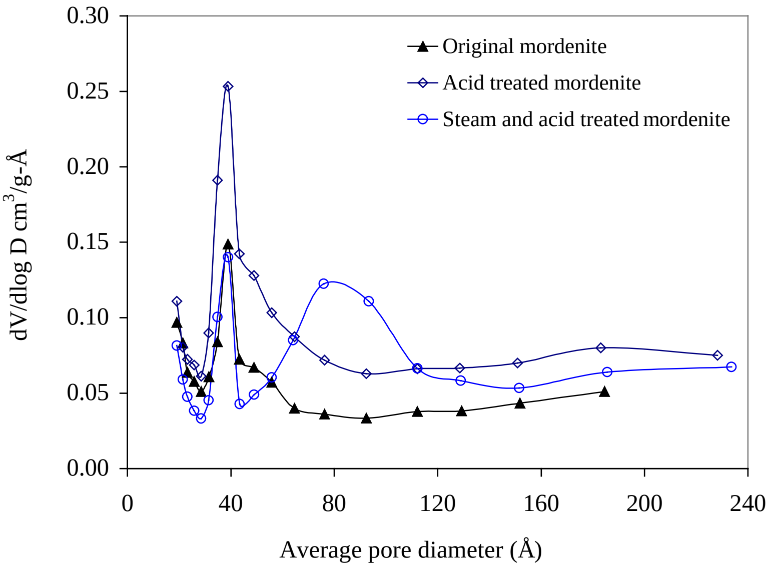

Fig. 1. Effects of dealumination on pore size distributions of mordenite.

Table 1
Characterization of catalyst supports and Pt-loaded precursors

Catalyst ID	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Meso + macropores (vol.%)	Average pore size (Å)	NH_3 (mmol/g)	Si/Al[a] ratio	Pt[a] (wt.%)
Mor	480	0.276	30.0	23.0	1.98	10.7	0.82
Mor(A)	466	0.295	40.6	25.4	0.55	34.2	0.96
Mor(S+A)	458	0.298	39.1	26.0	0.10	163.5	0.39
PILC	112	0.110	73.7	39.2	0.37	1.9	1.44
DILC	316	0.206	79.3	26.0	0.61	1.8	1.03
Al-MCM41	1001	0.950	100.0	45.0	0.13	16.2	0.97

[a] After loaded with Pt.

catalyst supports as well as the Si/Al ratio and the platinum content of the Pt-catalyst precursors are summarized in Table 1. The results indicate that aluminum content in mordenite was significantly decreased by acid treatment and the combination of steam and acid treatment. These treatments also reduced the acidity of the mordenite. The acidity of the catalyst supports was in the order: mordenite ≫ delaminated clay > acid treated mordenite > pillared clay > Al-MCM41 > steam and acid treated mordenite. Dealumination also reduced the available cation sites for platinum ion exchange, resulting in a much lower platinum content (0.39 wt.%) in steam and acid treated mordenite Pt/Mor(SA) than the target value (1 wt.%). Mordenite supports have the least amount of mesopores and macropores, while Al-MCM41 has the highest specific surface area, total pore volume, and the percentage of meso and macropores.

3.2. Hydrogenation and mild hydrocracking activities

The hydrogenation activity was expressed by the aromatics conversion, which was plotted versus the reaction temperature in Fig. 2. There exists a significant gap between mordenite based catalysts and other catalysts. Mordenite based catalysts (Pt/Mor, Pt/Mor(A) and Pt/Mor(SA)) exhibit the lowest aromatics conversions among all the catalysts tested. For mordenite based catalysts, aromatics conversion increases sharply with reaction temperature from 240 to 300 °C, then approached a plateau beyond 360 °C likely due

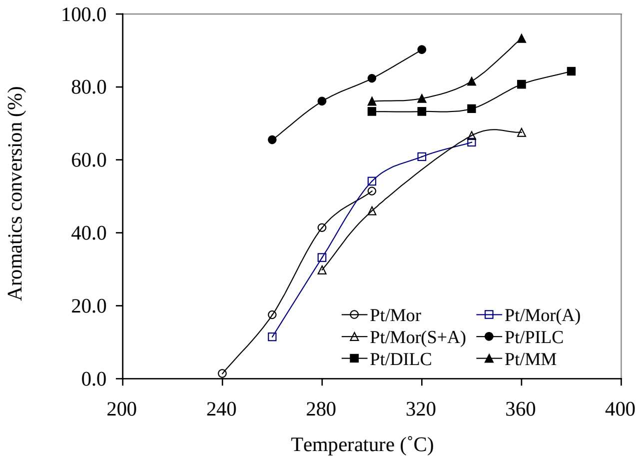

Fig. 2. Aromatics conversion as function of temperature (pressure: 10.3 MPa, LHSV: 1.0 h^{-1}, hydrogen flow: 600 NL/L feed).

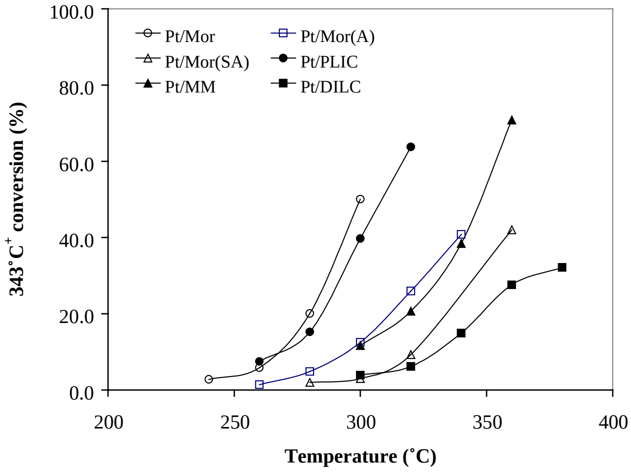

Fig. 3. Conversion of 343 °C$^+$ fraction as function of temperature (pressure: 10.3 MPa, LHSV: 1.0 h^{-1}, hydrogen flow: 600 NL/L feed).

to the hydrogenation/dehydrogenation equilibrium. Pillared clay based catalyst (Pt/PILC) had the same type of aromatic conversion–temperature curve as mordenite based catalysts with a much higher aromatics hydrogenation activity. Delamined clay (Pt/DILC) and Al-MCM41 (Pt/MM) based catalysts had similar aromatics conversion, and a plateau was observed for Pt/DILC beyond 380 °C. It is expected that the same plateau would occur for Pt/MM. The highest aromatics conversion was obtained over the Pt/MM catalyst (93.3% at 360 °C). The mild hydrocracking activity of the catalysts was expressed by the conversion of 343 °C$^+$ fraction, and was plotted against reaction temperature in Fig. 3. The results show that, among all the catalysts, the untreated mordenite based catalyst (Pt/Mor) had the highest hydrocracking activity and it required the lowest temperature to reach the same conversion of 343 °C$^+$ fraction. Excessive dealumination by the combination of steam and acid treatments rendered the catalyst (Pt/Mor(SA)) much less active as indicated by the higher temperature required converting the same amount of 343 °C$^+$ fraction. Delamined clay catalyst (Pt/DILC) had the lowest hydrocracking activity. In order to evaluate the overall catalyst performance for hydrogenation and mild hydrocracking, we summarized in Fig. 4 the aromatic conversion, naphtha and diesel yields (bar charts) at 30% conversion of 343 °C$^+$ fraction as well as the temperature (line chart) required to reach this conversion. The yields of naphtha (IBP—177 °C), diesel (177–343 °C) and 343 °C$^+$ fractions of the total liquid products were calculated using ASTM D2887 simulated distillation method. The best catalysts will be the ones that have high aromatic conversion, high diesel yield, low naphtha yield and relatively low 343 °C$^+$ fraction conversion temperature. Untreated mordenite, Pt/Mor was the most active cracking catalyst. However, it produced a substantially higher naphtha yield (25.4 wt.%) due to overcracking. Acid-treated mordenite catalyst, Pt/Mor(A), is not a good choice neither for the mild hydrocracking reaction due to its high naphtha and low diesel yields. Steam-and-acid-treated mordenite, Pt/Mor(SA), had lower naphtha and higher diesel yields, however, it required relatively high temperature (350 °C) to reach a 30% conversion of 343 °C$^+$ fraction. Delaminated clay Pt/DILC has the best diesel yield (67 wt.%) and naphtha yield (11.5 wt.%), but it is the least active cracking catalyst, requiring 363 °C to reach 30% conversion of 343 °C$^+$ fraction. This high temperature has some disadvantages such as higher power input, higher coke formation, and decline of aromatics hydrogenation rate due to thermodynamic equilibrium. Pillared clay Pt/PILC appeared to be a better catalyst than the delaminated clay. The temperature for 30% conversion of 343 °C$^+$ fraction is much lower (292 °C) than Pt/DILC-30, with only a marginal loss of diesel yield (64.9 wt.%) and slightly higher naphtha

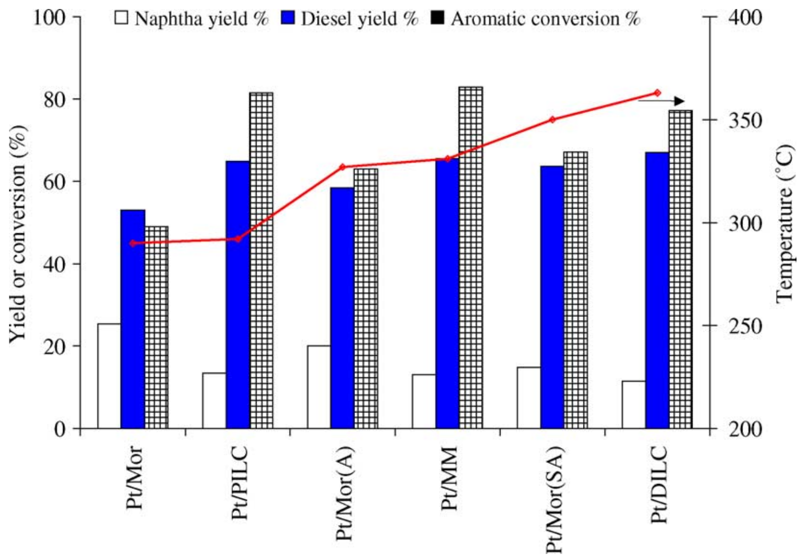

Fig. 4. Product distributions at 30% conversion of 343 °C$^+$ fraction (pressure: 10.3 MPa, LHSV: 1.0 h^{-1}, hydrogen flow: 600 NL/L feed).

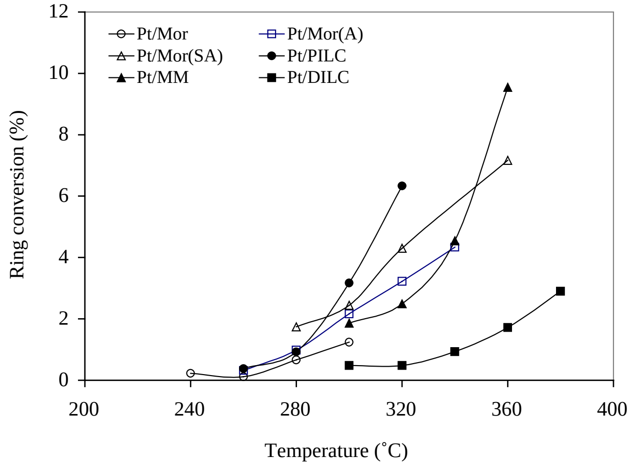

Fig. 5. Total ring compounds conversion as function of temperature (pressure: 10.3 MPa, LHSV: 1.0 h^{-1}, hydrogen flow: 600 NL/L feed).

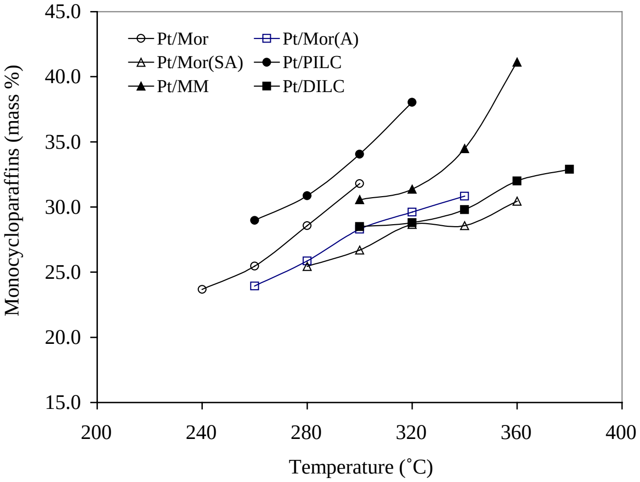

Fig. 6. Mass percentage of monocycloparaffins as function of temperature (pressure: 10.3 MPa, LHSV: 1.0 h^{-1}, hydrogen flow: 600 NL/L feed).

yield (13.5 wt.%). Finally, it is worth noting that Al-MCM41 mesoporous material based catalyst Pt/MM, is attractive as it had a reasonable reaction temperature (331 °C) to attain 30% conversion of 343 °C^+ fraction, and also had the second best diesel (65.5 wt.%) and naphtha yield (13.0 wt.%). Based on a compromise between low naphtha yield, high diesel yield, high aromatic conversion as well as low reaction temperature, Pt/PILC and Pt/MM are the best catalysts for aromatics hydrogenation and mild hydrocracking reactions. Both catalysts produced 65% diesel yield and over 80% aromatics conversion. Since Pt/PILC catalyst extrudates contain 30% of pseudo-böehmite as binder and 70% active ingredient as compared to 80% of pseudo-böehmite and 20% of active ingredient for Pt/MM catalyst extrudates, we could conclude that the intrinsic activity of Pt/MM is higher than that of Pt/PILC.

3.3. Ring opening activity

The ring opening activity of the catalysts was first evaluated by comparing the conversion of total ring compounds (monocycloparaffins, dicycloparaffins, tricycloparaffins and aromatics) using Eq. (3). Fig. 5 presents the conversion of total ring compounds versus temperature for each catalyst. The results indicate pillared clay (Pt/PILC) was the most active catalyst for converting the ring compounds. At 300 °C, the conversion decreased in this order: Pt/PILC > Pt/Mor(SA) > Pt/Mor(A) > Pt/MM > Pt/Mor > Pt/DILC. Figs. 6–8 plot the mass percentages of monocycloparaffins, dicycloparaffins and tricycloparaffins, respectively, in the total liquid products against the reaction temperature, to show how each saturated ring compound reacts. For all the catalysts, monoparaffin content increased with reaction

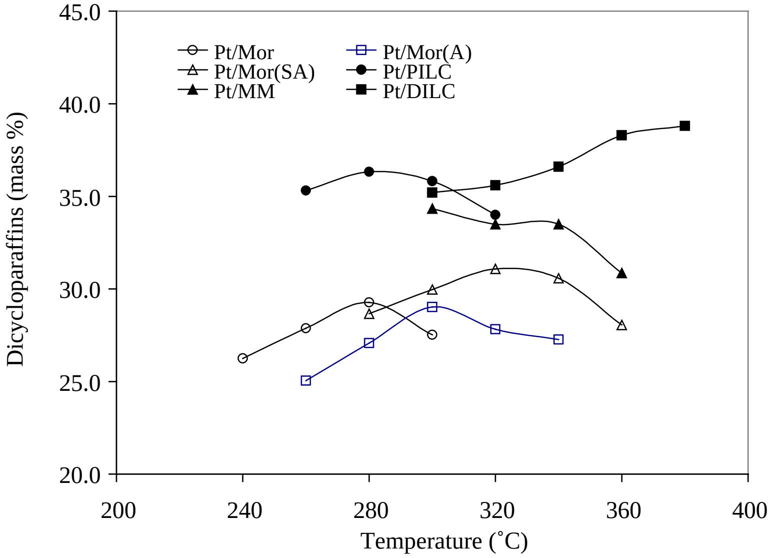

Fig. 7. Mass percentage of dicycloparaffins as function of temperature (pressure: 10.3 MPa, LHSV: 1.0 h^{-1}, hydrogen flow: 600 NL/L feed).

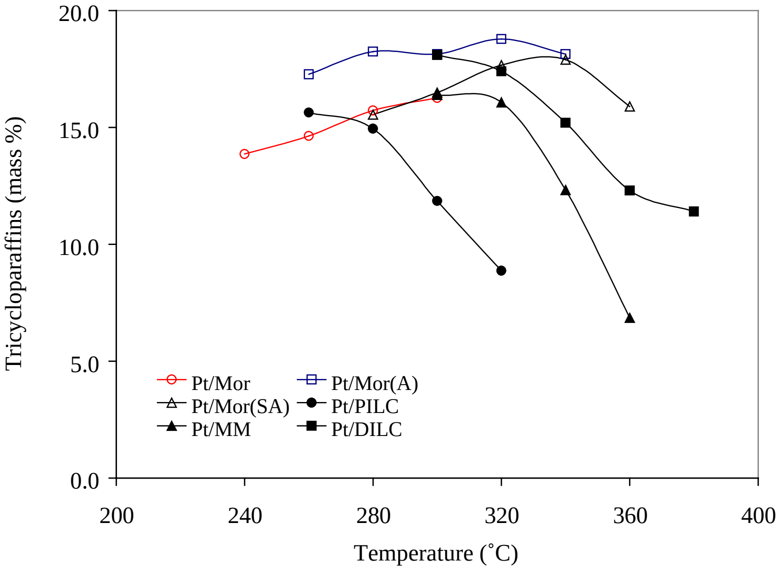

Fig. 8. Mass percentage of tricycloparaffins as function of temperature (pressure: 10.3 MPa, LHSV: 1.0 h^{-1}, hydrogen flow: 600 NL/L feed).

temperature (Fig. 6); dicycloparaffin content first increased with temperature, then decreased with temperature, with the exception of Pt/DILC (Fig. 7); similar to the dicycloparaffins, a maximum was observed over all the catalysts for tricycloparaffins with the exception of Pt/Mor, which showed a continuous increase of tricycloparaffins. Over Pt/DILC, the contents of tricycloparaffins showed a greater decrease with reaction temperature up to 360 °C. From 360 to 380 °C, the decrease slowed down probably due to the increasing rate of dehydrogenation (Fig. 8). These results indicated that dealuminated mordenite Pt/Mor(A) and Pt/Mor(SA), pillared clay (Pt/PILC), delaminated clay (Pt/DILC) and mesoporous molecular sieve (Pt/MM) have suitable pore structures and surface acidity to crack down the three-ring compounds. The untreated mordenite (Pt/Mor), being the most acidic catalyst support (Table 1), was unable to accommodate the three-ring compounds due to its smaller pore diameter. The results confirm that dealumination is a good way to create mesopores in mordenite support.

The ignition quality of a diesel fuel depends mainly on its chemical composition. In general, normal paraffins have the highest cetane numbers and, for the same carbon number, isoparaffins have lower cetane numbers, followed by moncycloparaffins, alkylbenzenes, polycycloparaffins and polyaromatics. The ignition qualities of the total liquid products were estimated by the IQT^{TM} method [11]. The cetane number of the feed measured by ASTM 613 engine method was 50.4, very close to the cetane number derived by IQT^{TM} (50.8). The data for catalysts at various temperatures are plotted in Fig. 9. The derived cetane numbers of the total liquid products obtained over all the mordenite-based catalysts were lower than that of the feed. Delaminated clay Pt/DILC gave the highest cetane number followed by mesoporous material Pt/MM and pillared clay Pt/PILC over the reaction temperature ranges.

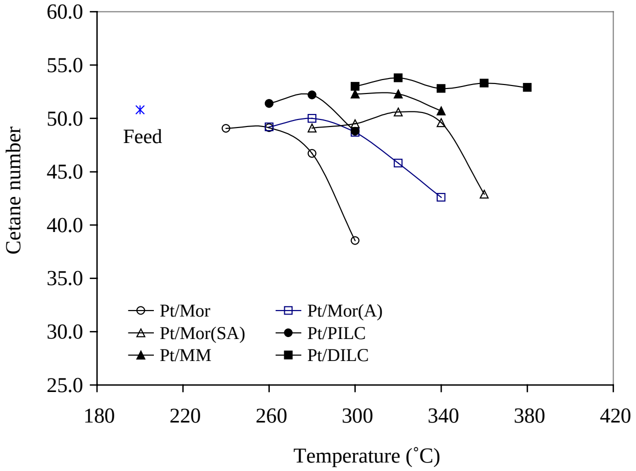

Fig. 9. Comparison of the ignition quality of total liquid products by IQT^{TM} test.

4. Discussion

Dealumination is an important way to modify pore size and surface properties of zeolite to promote various catalytic reactions [12,13]. Mordenite is not suitable for processing large molecules because of its uni-dimensional and non-intersecting channel system. However, modification of the structure by controlled dealumination presents opportunities for opening up the system. Our results showed that dealumination of mordenite, by either acid extraction or steam plus acid treatment, resulted in an increase of total pore volume and created mesopores and macropores (Fig. 1 and Table 1). These results are in agreement with other published papers [13–17]. Lee and Ha reported the modification of mordenite by HCl/steam treatment, and indicated that mesopores with diameter of 37 Å were developed as a result of dealumination [15]. In a study of comparison of mordenite dealumination by nitric acid and oxalic acid, Guidici et al. revealed that there was formation of additional volume in pores 20 and 600 Å as well as some macropores >600 Å when the mordenite was leached by nitric acid, while the texture of the sample treated with oxalic acid remained unchanged [17]. The formation of mesopores during dealumination can be explained by two mechanisms: (1) the vacancies left by Al expelled from the framework are not completely filled by the slow migration of Si, thus producing a local defect in the crystal structure; (2) due to extended dealumination, some zeolite crystals collapse and the collapsed zeolite is removed by acid leaching, resulting in the formation of channels and cracks in the mordenite. Furthermore, it is possible that acid treatment removes some of the framework Al in 4-membered rings, as well as amorphous material stacked inside the mordenite, making the 8-membered ring channels more accessible and allowing easier diffusion from the main 12-membered ring channels. Our results also indicated that the acidity of the mordenite as measured by NH_3-TPD method decreased gradually with increase of aluminum-removal (Table 1). Meyers et al. observed the same reduction trend of the acidity over thermal, acid and thermal/acid treated mordenite by NH_3-TPD [18]. However, acidity measured by *t*-butylamine-TPD revealed a different pattern, despite the reduction of aluminum content, more *t*-butylamine was adsorbed on the acid and thermal/acid treated mordenite. The authors suggested that acid extraction dissolved the nonframework silica-alumina from the zeolite pore and increased the accessibility of the acid sites to *t*-butylamine [18]. We believe that the creation of meso and macropores also increases the diffusivity of *t*-butylamine and larger molecules within zeolite structure. The results of the conversion of cycloparaffins over the three mordenite based catalysts support this theory. Over the three catalysts, the yields of paraffins and monocycloparaffins increased with reaction temperature. Paraffins can be produced by cracking the side chains of aromatics and cycloparaffins. They can also be produced by opening saturated rings of naphthenes. Monocycloparaffins are produced mostly from saturation of monoaromatics and ring opening of di- or tricycloparaffins. The amount of dicycloparaffins first increased with reaction temperature, reached a plateau, and then decreased. This result indicates that all three catalysts are capable of converting molecules as large as two-ring cycloparaffins. Dicycloparaffins are derived from tricycloparaffins by ring opening, and from diaromatics by hydrogenation reactions. For the mass percentage of tricycloparaffins, maxima were observed over acid treated mordenite (Pt/Mor(A)) and steam plus acid treated mordenite (Pt/Mor(S+A)). However, tricycloparaffin content continuously increased with temperature over the untreated mordenite catalyst (Pt/Mor) in the temperature range used, which indicated that it was unable to convert molecules as large as tri-ring naphthenes. The reduction in diffusion resistance over aluminum deficient mordenite was observed by several research groups [14,19,20]. As early as 1970, Eberly Jr. and Kimberlin Jr. from Esso Research Laboratories reported that the modenite with a SiO_2/Al_2O_3 ratio of 64 prepared by HCl treatment had higher adsorption capacity, lower diffusion resistance and higher cracking activity for cumene molecules than the conventional untreated mordenite [20]. Recently, Tromp et al. from the University of Utrecht studied the influence of HCl acid leaching on the hydroisomerization of *n*-hexane over Pt/mordenite. Their results demonstrated that the activity of the untreated mordenite was limited by mass transfer effects, those effects almost vanished after modification of the mordenite by acid leaching, which generated a 3D micropore structure as well as mesopores. The reduction of the acidity in mordenite by dealumination allows the mild hydrocracking to be carried out at a higher reaction temperature without producing significant amounts of naphtha and gaseous products due to over cracking. Therefore, it seems by dealumination of mordenite, catalysts with an optimum balance of pore size and acidity can be obtained for the hydrogenation and mild hydrocracking of middle distillates.

Layered clays, such as montmorillonite can swell and expand in one dimension through the process of intercalation using pillaring agents [21]. This property allows pillared clays to be used in a number of potential applications in petroleum refining [22–24]. In this study, pillared montmorillonite was prepared by ion-exchange of Na^+ cations with large polyoxocations of aluminum [7]. The resultant material after calcination contained oxide pillars that open the sheets and expose the internal surface of the clay layers. Pillared montmorillonite has a special slit-shape geometry that presents excellent shape selectivity for processing planar molecules such as aromatic compounds. The higher selectivity towards aromatic saturation of Pt/PILC over other catalysts observed in this work (Fig. 4) further confirmed the suitability of its structure to facilitate the adsorption and reaction of aromatic compounds between the sheets of the layered clay. The pillars formed within the interlamellar space also provide acid sites for hydrocracking. The acid sites in pillared clay are mostly Lewis sites, which is a less active cracking component than the Brønsted acidity found in zeolites. The difference in acid sites is probably why Pt/PILC produce much less naphtha (13.5 versus 25.4 wt.%) than Pt/Mor at 30% conversion of $343\,^{\circ}C^+$ fraction and at the same temperature (∼290 °C).

Delaminated clays have disordered edge-to-edge and face-to-edge aggregations (house-of-cards type structures) when compared with the ordered stacking arrangement or face-to-face aggregations in pillared clays. In addition to micropores found in pillared clay, delaminated clays also contain mesopores and macropores that are formed from face-to-edge aggregations [25–27]. Although, the delaminated clay based catalyst (Pt/DILC), had the second highest acidity of the six catalysts measured by NH_3-TPD, it had the lowest cracking activity and required the highest temperature to reach 30% conversion of $343\,^{\circ}C^+$ fraction

(Fig. 3). Using pyridine/FTIR adsorption studies, Occelli claimed that the strength of acid sites in delaminated Laponite was weaker than those found in pillared clay [25]. He attributed the weaker acidity and reduced cracking activity of the delaminated clay to differences in the availability of acid sites resulting from stacking disorders. The discrepancy between pyridine and NH_3 measurements may be due to the difference in molecular size and diffusion rates of these two molecules. Our previous results suggested that the delaminated clay used in this work had higher density of pillars inserted between its sheets than the pillared montmorillonite used, which could be responsible for the large amount of NH_3 adsorbed [7]. However, due to the random house-of-cards structure, some of the acid sites in the pillars could be buried, and only accessible to small molecules such as NH_3 and not to larger molecules such as pyridine. Accordingly, in the hydrogenation and hydrocracking study, these pillars were less available to the large gas oil molecules, resulting in a lower cracking rate.

Since their discovery by Mobil researchers, mesoporous molecular sieves with tunable pore structure and high surface area are beginning to find application in the area of catalysis and environmental protection [28–30]. Compared with microporous zeolite materials, which often suffer from diffusion limitations due to size of the molecules, mesoporous molecular sieves have the advantages of larger pore diameters, higher adsorption capacities and higher surface areas, which make them very attractive for processing petroleum fractions. Corma et al. compared the aromatic saturation activities of Pt/Al-MCM-41, Pt/amorphous mesoporous silica–alumina, Pt/amorphous silica–alumina and Pt/USY zeolite catalysts in a batch reactor at 5.0 MPa using a hydrotreated light cycle oil [28]. The highest hydrogenation activity was observed over Pt/Al-MCM-41 catalyst. At 300 °C, the total aromatic conversions were 40.3 and 23.4% for Pt/Al-MCM-41 and Pt/USY, respectively. The authors suggested that the high hydrogenation activity of Pt/Al-MCM-41 was due to its very high surface area that allowed better dispersion of the Pt particles [30]. Higher hydrogenation activity was also observed in our study for Pt/MM compared with mordenite based catalysts. Over 80% of aromatics were converted over Pt/MM at 331 °C, 10.3 MPa, $1.0\,h^{-1}$ LHSV compared to 63% over Pt/Mor(A) at 350 °C. The incorporation of aluminum into the MCM41 framework created an acidic cracking function and made it a hydrocracking catalyst. In this work, although the NH_3-TPD results (Table 1) showed that Al-MCM-41 based catalyst (Pt/MM) had similar acidity to steam and acid treated mordenite based catalyst (Pt/Mor(SA)), it had much higher mild hydrocracking activity than Pt/Mor(SA) (Fig. 4). The difference in the hydrocracking activity was due to the mesoporous structure of Pt/MM and the microporous structure of Pt/Mor(SA). It is clear that larger pore materials have more potential as catalysts for processing bulk molecules.

5. Conclusions

Six catalysts belonging to four categories of materials have been tested for their hydrogenation and mild hydrocracking activities on a middle distillate from Canadian oil sands. The results showed that, due to its microporus structure and strong acidity, untreated mordenite based catalyst gave high naphtha yield at the expense of the diesel fraction, and was not suitable for mild hydrocracking. Dealumination made mordenite a better mild hydrocracking and ring opening catalyst due to the reduction of acidity and the creation of meso and macropores. However, mordenite based catalysts had the lowest hydrogenation activities among the four types of materials studied. Delaminated clay catalyst, despite having high hydrogenation activity and diesel yield, required the highest activation temperatures. Based on a compromise between low naphtha yield, high diesel yield, high aromatic conversion as well as low reaction temperature, Al-MCM41 and pillared clay were the best catalysts in our reaction conditions, which presented high aromatic conversions, a reasonable temperature to reach 30% conversion of $343\,^{\circ}C^{+}$ fraction and high diesel yields.

Acknowledgements

Partial funding for this work has been provided by the Canadian Program for Energy Research and Development (PERD), the Alberta Research Council and The Alberta Energy Research Institute. The authors gratefully acknowledge NCUT pilot plant staff for operating the hydrotreating unit, and NCUT analytical laboratory staff for determining the feed and product properties. The editorial assistance of Norman Sacuta is greatly appreciated.

References

[1] H.H. Wu, M.E. Reno, G.R. Brierley, in: Proceedings of the AIChE Spring National Meeting, Hydrocracking Technology and Applications Symposium, Session 57, New Orleans, LA, February 25–29, 1996, Paper 57C.

[2] E.P. Dai, C.N. Campbell, in: I.M.C. Oballa, S.S. Shih (Eds.), Catalytic Hydroprocessing of Petroleum and Distillates, Marcel Dekker, New York, 1994, p. 127.

[3] H. Kosslick, G. Lischke, B. Parlitz, W. Storek, R. Frichke, Appl. Catal. A 184 (1999) 49.

[4] J. Weitkamp, S. Emst, H.G. Karge, Erdoel Kohle-Erdgas-Petrochem. 370 (1984) 457.

[5] H. Yang, M. Wilson, C. Fairbridge, Z. Ring, Am. Chem. Soc., Div. Petro. Chem. 47 (1) (2002) 93 (Preprint).

[6] H. Yang, M. Wilson, C. Fairbridge, Z. Ring, J. Hill, Energ. Fuel. 16 (2002) 855.

[7] H. Yang, C. Fairbridge, Z. Ring, R. Hawkins, J. Hill. Stud. Surf. Sci. Catal. 141 (2002) 543.

[8] C.J. Guo, C.W. Fairbridge, J.-P. Charland, US Patent 5,538,710 (1996).

[9] C.J. Robinson, G.L. Cook, Anal. Chem. 41 (1969) 1548.

[10] C.J. Robinson, Anal. Chem. 43 (1971) 1425.

[11] L.N. Allard, G.D. Webster, T.W. Ryan, G. Baker, A. Beregszaszy, C.W. Fairbridge, A. Ecker, J. Rath, SAE Technical Paper Series, Society of Automotive Engineers, Warrendale, PA, 1999, Paper No. 3591.

[12] J. Scherzer, ACS Symp. Ser. 248 (1984) 157.

[13] A.W. O'Donovan, C.T. O'Connor, K.R. Koch, Micropor. Mater. 5 (1995) 185.

[14] M. Tromp, J.A. van Bokhoven, M.T. Garriga Oostenbrink, J.H. Bitter, K.P. de Jong, D.C. Koningsberger, J. Catal. 190 (2000) 209.

[15] K.H. Lee, B.H. Ha, Micropor. Mesopor. Mater. 23 (1998) 211.

[16] C. Choi-Feng, J.B. Hall, B.J. Huggins, R.A. Beyerlein, J. Catal. 140 (1993) 395.

[17] R. Giudici, H.W. Kouwenhoven, P. Prins, Appl. Catal. A 203 (2000) 101.

[18] B.L. Meyers, T.H. Fleisch, G.J. Ray, J.T. Miller, J.B. Hall, J. Catal. 110 (1988) 82.

[19] R. Beecher, A. Voorhies Jr., P. Eberly Jr., Ind. Eng. Chem. Prod. Res. Dev. 17 (1968) 203.

[20] P.E. Eberly Jr., C.N. Kimberlin Jr., Ind. Eng. Chem. Prod. Res. Dev. 9 (1970) 335.

[21] F. Figueras, Catal. Rev. Sci. Eng. 30 (1988) 457.

[22] H. Ming-Yuan, L. Zhonghui, M. Enze, Catal. Today 2 (1988) 321.

[23] N. Kimbara, J.P. Charland, M.F. Wilson, Ind. Eng. Chem. Res. 35 (1996) 3874.

[24] M.L. Occelli, R.J. Rennard, Catal. Today 2 (1988) 309.

[25] M.L. Occelli, Catal. Today 2 (1988) 339.

[26] T.J. Pinnavaia, M.S. Tzou, S.D. Landau, R.H. Raythatha, J. Mol. Catal. 27 (1984) 195.

[27] M.L. Occelli, S.D. Landau, T.J. Pinnavaia, J. Catal. 104 (1987) 331.

[28] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.

[29] K.M. Reddy, C.S. Song, Catal. Today 31 (1996) 137.

[30] A. Corma, A. Martínez, V. Martínez-Soria, J. Catal. 169 (1997) 480.