Hydroisomerization of *n*-hexadecane over Pt/Al-MCM-41 catalysts: Two different Al incorporation methods

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The hydroisomerization of *n*-hexadecane was carried out over Pt/Al-MCM-41 catalysts at 350°C and 103 bar. Al-MCM-41 was prepared by two different methods; a direct sol-gel method (Pre) and a post-grafting method (Post). Al-MCM-41 was characterized by using XRD, nitrogen adsorption, ^{27}Al NMR and ammonia TPD. Pt/Al-MCM-41-Post showed higher conversions and higher isomerization yield than Pt/Al-MCM-41-Pre. This difference was attributed to the better accessibility of tetrahedral sites (Broensted acid sites) in Al-MCM-41-Post than those in Al-MCM-41-Pre.

1. INTRODUCTION

Removal of long-chain *n*-alkanes, dewaxing, is essential for the acceptability of lubricating oils. The isomerization of *n*-alkanes is favorable for the production of higher quality oil in higher yield than hydrocracking of *n*-alkanes. Bifunctional catalysts comprising metal sites for hydrogenation/dehydrogenation and acid sites for C-C rearrangement are effective for *n*-alkane isomerization. In our previous work [1], the catalytic performance in *n*-hexadecane hydroisomerization over bifunctional platinum catalysts containing ZSM-5, ZSM-22, SAPO-11, H-Y, H-***b*** and Al-MCM-41 was investigated. Among the catalysts, Pt/Al-MCM-41 catalysts showed the highest isomerization selectivity as well as the highest yield of multibranched isomers, presumably not only due to its moderately weak acidity and mesoscale pores but also due to higher platinum dispersion.

The acidity of the catalysts has a major effect on hydrocracking and hydroisomerization. Purely siliceous MCM-41 has no Broensted acidity, but isomorphous substitution of Si by a trivalent cation such as Al or Ga creates moderately acidic sites. Recently, various routes have been developed for Al incorporation into the framework of MCM-41 [2-6]. These Al incorporation methods influence the nature of Al-MCM-41 such as concentration of acid sites, pore structure and surface area. This study is aimed at investigating the catalytic performance in *n*-hexadecane isomerization over Pt/Al-MCM-41 whose aluminum was introduced by two different Al incorporation methods; a direct sol-gel method (designated as Pre) and a post-synthetic grafting method (designated as Post).

2. EXPERIMENTAL

2.1. Preparation of Al-MCM-41

2.1.1. Direct hydrothermal synthesis of Al-MCM-41-Pre

Cetyltrimethylammonium chloride (25% CTACl, Aldrich) was dissolved in distilled water. The silica source, Ludox HS-40 (DuPont) was then added dropwise to the template solution

with vigorous stirring at 70°C in a water bath. The aluminum source - pseudoboehmite (78.2% Al_2O_3, Vista), $NaAlO_2$ (31% Na_2O, 37% Al_2O_3, Junsei) or aluminum isopropoxide (98%, Aldrich) - was added into the hydrogel, and was designated as Pre-P, Pre-N, Pre-A, respectively. The molar composition of mixture gel was $1.0CTACl:1.0Na_2O:4.0SiO_2:400H_2O$, and the Si/Al ratios were taken to be 5, 10, 20 and 40. The pH of mixture was maintained at 10.0 with 5wt.% acetic acid after heating at 100°C for 2 days, and this pH adjustment was repeated twice more. The product was filtered, washed, dried in air and calcined at 550°C for 10 h. To obtain proton-exchanged Al-MCM-41-Pre, the calcined Al-MCM-41-Pre was ion-exchanged twice with 1M NH_4Cl solution at 70°C for 10 h, and calcined at 550°C for 10 h. Purely siliceous MCM-41 supports were prepared by the same procedure but without adding Al source to the preparation mixture.

2.1.2. Post-synthesis modification for Al-MCM-41

Al-MCM-41-Post was prepared by incorporating aluminum to siliceous MCM-41 support by post-synthetic metal incorporation method. Siliceous MCM-41 was heated to remove water in a vacuum oven at 100°C for 10 h. $AlCl_3$ (98%, Junsei) in absolute ethanol (99.8%, Merck) was added to MCM-41 in a propylene bottle and the mixture was stirred vigorously for 30 min. The mixture was filtered, washed and dried at 110°C in air, and calcined at 550°C for 10 h. After calcination, Al-MCM-41-Post with Si/Al=5, 10, 20, 40 was obtained.

2.1.3. Platinum impregnation

Platinum was loaded to get the different content (0.01 to 0.5wt.%) with $Pt(NH_3)_4Cl_2$ (98%, Aldrich) solution by excess water evaporation. After impregnation, the materials were dried at 110°C for 5 h and calcined at 320°C for 2 h.

2.2. Characterization

The powder X-ray diffraction (XRD) patterns of MCM-41 supports were recorded on a Rigaku Miniflex using Cu Kα radiation at 40 kV and 45 mA. The acidic property of molecular sieves was analyzed by TPD (temperature programmed desorption) of chemisorbed ammonia. A 0.01 g of sample was placed in a quartz tubular reactor and pretreated in a helium flow, heated to 300°C with 10°C/min, and remained at 300°C for 2 h. The samples were cooled to 100°C and ammonia pulse was injected five times. After physisorbed ammonia was purged with helium, TPD was carried out. BET surface area, pore volume and pore size distribution were calculated from N_2 adsorption/desorption isotherms at liquid N_2 temperature using a Micromeritics ASAP2000. ^{27}Al solid NMR spectrum obtained at 78.2 MHz was analyzed to investigate the Al environment in Al-MCM-41 by using FT NMR spectrometer with MAS (Bruker AM-400) and chemical shifts were recorded with respect to $[Al(H_2O)_6]^{3+}$.

2.3. Model reaction

The catalytic conversion of *n*-hexadecane was carried out in a batch reactor of 300 ml (EZE-Seal, Autoclave Engineers). A 0.5 g of catalyst was loaded in the reactor and then hydrogen was introduced with 50 ml/min to reduce Pt at 350°C and 500 rpm for 2 h. The reactor was cooled to 50°C, fed with 50 ml of *n*-hexadecane and pressurized to 34.5 bar with hydrogen. The impeller was set to 1000 rpm. The reactor was gradually heated at a rate of 5 °C/min to 350 °C and pressure was set to 103 bar. The liquid products were analyzed by HP 6890A gas chromatograph equipped with a FID and a 50 m capillary column (HP-1) to identify the unreacted feed, the isomerized and the cracked products.

3. RESULTS AND DISCUSSION

The high temperatures during calcination or under process conditions lead to disruptions in the framework and to the subsequent collapses of pores and channels in the molecular sieves when too much Al is incorporated. Fig. 1 shows the XRD patterns of calcined MCM-41 and Al-MCM-41 supports. The samples revealed relatively well-defined XRD patterns identical to those reported for MCM-41 materials [2-4]. The intensity of (100) plane of MCM-41 decreased in the order of MCM-41 > Al-MCM-41-Post > Al-MCM-41-Pre-A > Al-MCM-41-Pre-P > Al-MCM-41-Pre-N. The higher the Si/Al of Al-MCM-41 was, the higher was the intensity of XRD pattern obtained.
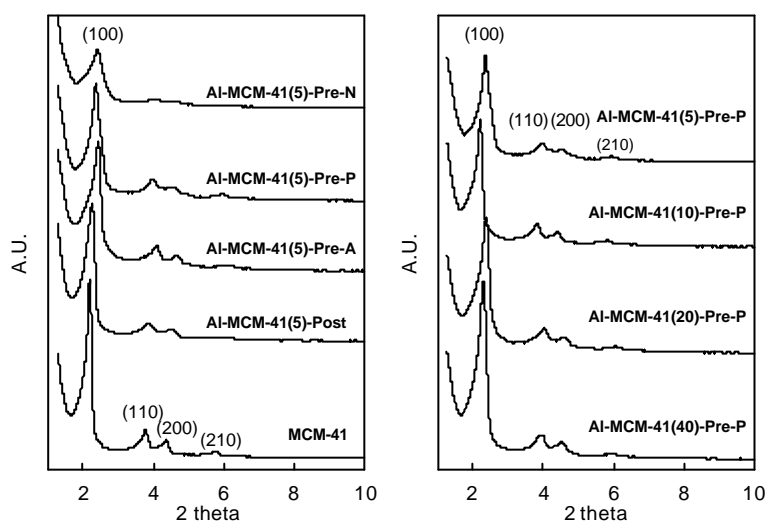

Fig. 1. XRD patterns of calcined MCM-41 and Al-MCM-41 supports.

The structural properties of supports are given in Table 1. The structure of MCM-41 is hexagonal and unit cell parameter can be calculated from the equation $a_o=2d_{100}/\sqrt{3}$. MCM-41 supports have high surface area (750-1280 m^2/g), average pore diameter (ca. 30 Å) and wall thickness (10-15 Å). The surface areas of all Al-MCM-41 supports slightly decreased with Al content. As the amount of aluminum incorporated increased, the pore volume and average pore volume of Al-MCM-41-Pre generally decreased. This is probably due to partial collapse of the hexagonal structure on removing the template and is caused by the instability associated with the presence of increasing amounts of framework aluminum. Al-MCM-41-Post has more uniform pore diameter and higher wall thickness than Al-MCM-41-Pre, indicating that grafting method allows the preparation of structurally well-ordered materials in high Si/Al.

Lubricating oils of good quality should have lower pour points and higher viscosity indexes. Effective hydrodewaxing catalysts should produce high yields of isoalkanes from *n*-alkanes. Multibranched isoalkanes have the advantage of lowering the pour point and the disadvantage of being susceptible to cracking, resulting in a yield loss. The catalysts with high hydrogenation ability and moderate acidity are desirable for the hydroisomerization of long chain hydrocarbons [1,7].

Fig. 2 shows the temporal conversions of *n*-hexadecane over Pt/Al-MCM-41 with Si/Al=5 catalysts. The catalytic activity decreased in the order of Pt/Al-MCM-41-Post > Pt/Al-MCM-

Table 1
Structural properties of MCM-41 and Al-MCM-41 supports.

Supports	d_{100} (Å)	a_o (Å)	S_{BET} (m^2/g)	Pore vol.(ml/g)	Pore dia. (Å)	Wall thickness (Å)
MCM-41	40.1	46.3	1280	1.15	31.1	15.2
Al-MCM-41(5)-Pre-A	36.6	42.3	760	0.76	29.5	12.8
Al-MCM-41(5)-Pre-N	36.6	42.3	750	0.70	29.0	13.3
Al-MCM-41(5)-Pre-P	40.3	46.5	1010	0.96	33.6	12.9
Al-MCM-41(10)-Pre-P	39.6	45.7	1100	0.97	33.3	12.4
Al-MCM-41(20)-Pre-P	39.3	45.4	1130	1.40	34.0	11.4
Al-MCM-41(40)-Pre-P	38.7	44.7	1190	1.42	34.7	10.0
Al-MCM-41(5)-Post	39.9	46.1	1040	0.92	31.1	15.0
Al-MCM-41(10)-Post	40.1	46.3	1090	0.92	31.4	15.1
Al-MCM-41(20)-Post	40.1	46.3	1110	1.00	31.0	15.3
Al-MCM-41(40)-Post	39.9	46.1	1140	1.02	30.7	15.2

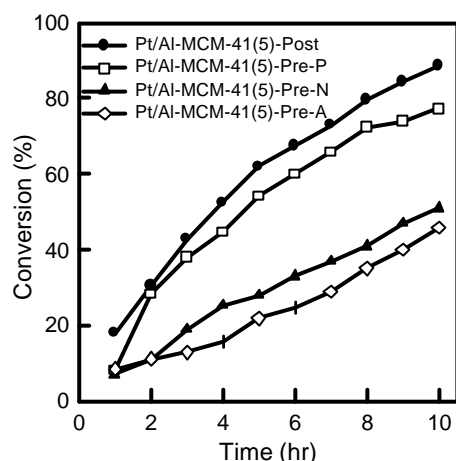d_{100}: d-spacing of (100), a_o: unit cell parameter

Fig. 2. Temporal conversion of *n*-hexadecane over 0.5wt%Pt/Al-MCM-41(5) catalysts at 350°C and 103bar.

41-Pre-P > Pt/Al-MCM-41-Pre-N > Pt/Al-MCM-41-Pre-A. The catalytic activities over Pt/Al-MCM-41-Pre-P and /Al-MCM-41-Post catalysts with Si/Al are shown in Fig. 3. The lower the Si/Al ratios (higher amount of Al) of Al-MCM-41 supports were, the higher were the conversions obtained. The conversions over Pt/Al-MCM-41-Post catalysts were higher than those over Pt/Al-MCM-41-Pre. The difference in conversion between Pt/Al-MCM-41-Post and Pt/Al-MCM-41-Pre was larger in higher Si/Al ratio of Al-MCM-41. The product distributions of Pt/Al-MCM-41-Pre and Pt/Al-MCM-41-Post catalysts are shown in Fig. 4. The fractions below the thick line represent the selectivity to hydroisomerization, while those over the thick line the selectivity to hydrocracking. The products were mostly isohexadecanes including mono-, di- and tri- branched isohexadecanes at conversions below 80%,
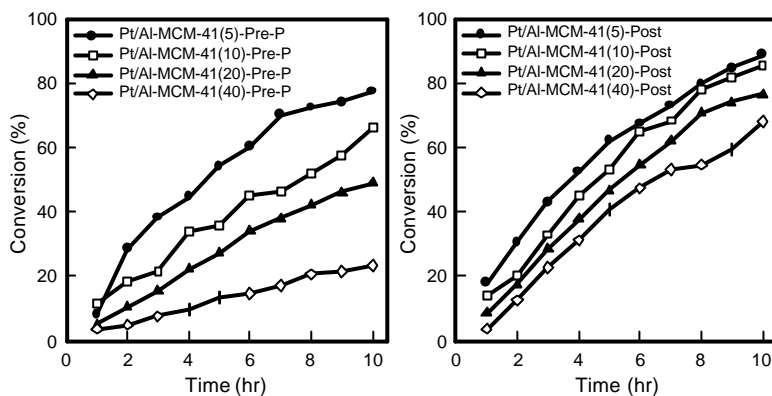
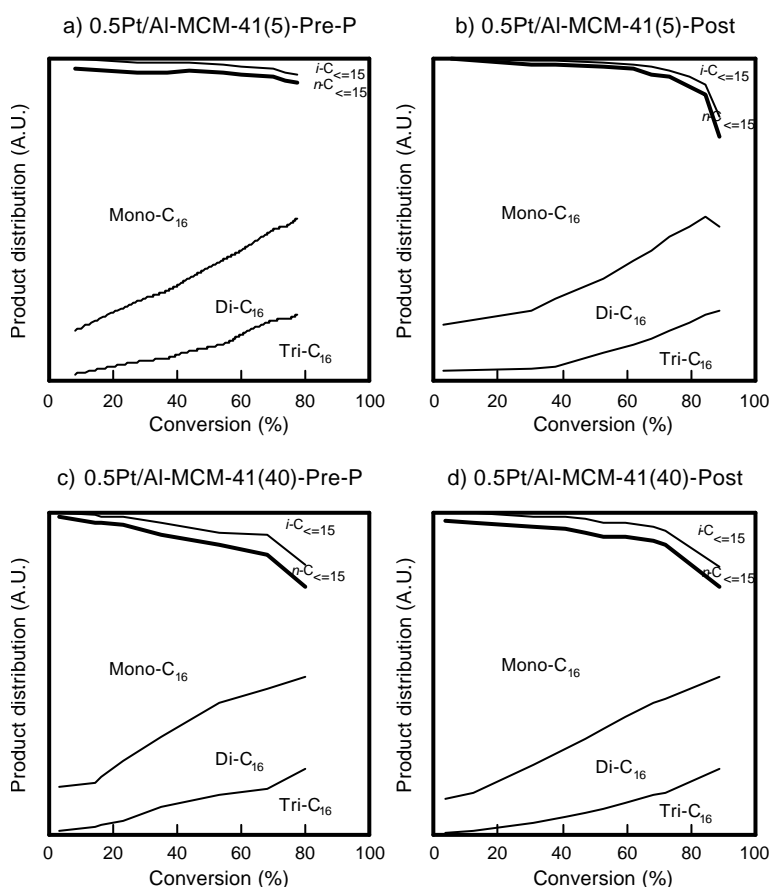Fig. 3. Temporal conversion of *n*-hexadecane over 0.5wt%Pt/Al-MCM-41-Pre and Pt/Al-MCM-41-Post catalysts with different Si/Al at 350°C and 103bar.

Fig. 4. Product distribution over 0.5wt%Pt/Al-MCM-41-Pre and Pt/Al-MCM-41-Post catalysts at 350°C and 103bar.

and the selectivity of branched isohexadecanes marked up to 98 wt.% at 50% conversion. Di- and tri-branched isohexadecanes were formed due to the mesoscale pores of Al-MCM-41. The fractions of di-branched and tri-branched isohexadecanes increased with conversion. Accordingly, the fraction of monobranched isohexadecanes decreased, since mono-branched isohexadecanes were consecutively converted to di- and tri-branched isohexadecanes. Even if di- and tri-branched isohexadecanes are susceptible to cracking, the hydrocracking was not that significant up to a conversion of 70%. At higher conversions over 70%, however, hydrocracking became significant.

The amount of Broensted acid sites of Al-MCM-41 measured by isopropylamine TPD were in accordance with the acid amount by NH_3 TPD. Fig. 5 illustrates the TPD profiles of ammonia over Al-MCM-41 supports. For Al-MCM-41, the curve shows a gradual rise to a maximum at 230-260°C (mild acidity compared with ZSM-5) and thereafter declines. It can be seen that Al-MCM-41-Post had higher content of acid sites than Al-MCM-41-Pre at the same Si/Al ratios, and that the amount of acid sites of Al-MCM-41 increased with decreasing Si/Al ratios as expected.

The ^{27}Al MAS NMR spectra (not shown) of the supports show signal at 53 ppm due to tetrahedrally coordinated framework aluminum, Al(IV), and 0 ppm caused by octahedrally coordinated Al sites, Al(VI) at extra-framework. The tetrahedral Al sites can be regarded as Broensted acid sites. The signal appeared at 30 ppm is related to the deformation of some tetrahedral Al sites. Table 3 shows the percent of tetrahedral Al(IV) sites in Al-MCM-41 supports obtained from ^{27}Al NMR spectra. The Al(IV) sites were predominant for Al-MCM-41-Pre before calcination, but the Al(VI) sites were formed after calcination, with a concomitant decrease of the Al(IV), indicating some extent of aluminum decomposed from the Al-MCM-41 framework. For Al-MCM-41-Post, the percent of Al(IV) sites was relatively low before calcination, but the percent of Al(IV) sites became significant after calcination, being in evidence that aluminums were successfully incorporated into the framework of MCM-41 through calcination. Ammonia TPD data suggest that Al-MCM-41-Post contained
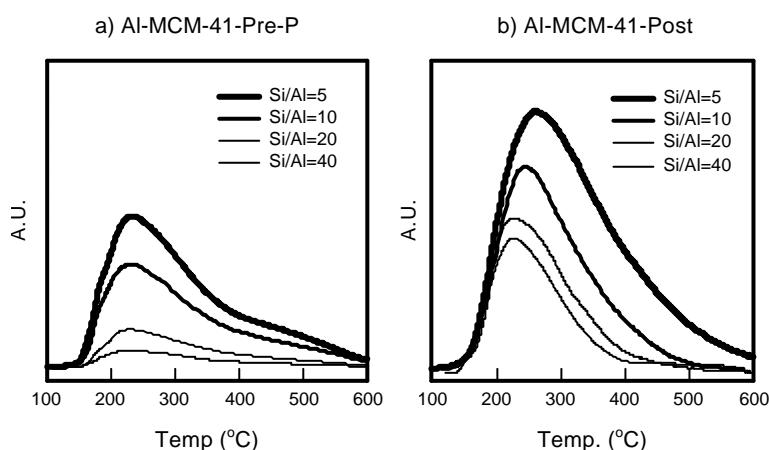

Fig. 5. Ammonia TPD of Al-MCM-41-Pre and -Post supports.

Table 2
Tetrahedral Al(IV) sites for Al-MCM-41 from solid ^{27}Al MAS NMR.

Si/Al	Al-MCM-41-Pre-P		Al-MCM-41-Post	
	% Al (IV) before calcination	% Al (IV) after calcination	% Al (IV) before calcination	% Al (IV) after calcination
5	100	65.8	27.1	57.0
10	100	73.0	25.3	53.1
20	100	65.4	39.7	46.1
40	100	67.4	45.0	48.5

higher content of acid sites than Al-MCM-41-Pre, whereas Al NMR results indicate that the amount of tetrahedral sites (Broensted acid sites) of Al-MCM-41-Pre was larger than that of Al-MCM-41-Post. As aluminum of Al-MCM-41-Pre was introduced in the preparing step of hydrogel, aluminum would be located uniformly at any position (outer or inner) in Al-MCM-41 in view of the ionic radius of Al^{3+} (0.57 Å). Significant portion of inner Al sites were buried in the framework and became inaccessible. On the other hand, Al(IV) sites in Post-catalysts seem to be located mostly at the accessible outer sites. Reaction data did not agree with NMR results but with TPD results. Accordingly, this discrepancy between NMR and TPD seems to be attributed to the different accessibility of Al(IV) sites due to the thick wall (about 10-15 Å) of MCM-41.

The selectivity in the hydroisomerization of *n*-hexadecane over Pt/Al-MCM-41-Pre and -Post catalysts is summarized in Table 3. At around 50% conversions, all Pt/Al-MCM-41 catalysts showed high isomerization selectivity of more than 90 weight percent. It seems that hydroisomerization is favorable than hydrocracking, due to the mild acidity of Al-MCM-41. Among the catalysts, Pt/Al-MCM-41(5)-Post catalyst showed the highest isomer yield, concomitantly the lowest hydrocracking selectivity. The higher the acid concentration of Al-MCM-41 support was, the higher the conversion and isomerization yield were obtained over the Pt/Al-MCM-41 catalysts.

Temporal conversion and selectivity over Pt/Al-MCM-41(5)-Post with different Pt loadings are shown in Fig. 6. The conversion and hydroisomerization yield increased with Pt loading. The conversion over Al-MCM-41 catalyst with 0.01 wt.% of Pt was slightly higher than that of Al-MCM-41 catalyst with no metal loading. Pt impregnation of 0.05 wt.% could make the conversion to increase drastically. It should be noted that even a small amount of Pt impregnation could change the product distribution from the pattern of cracking to that of hydroisomerization.

Table 3
Product selectivity for hydroisomerization of *n*-hexadecane over Pt/Al-MCM-41 catalysts.

Catalysts*	Conversion (%)	B-C_{16} sel. (wt%)	Mono-C_{16}	Di-C_{16}	Tri-C_{16}	Cracking sel. for $C_{\leq=15}$
Pt/Al-MCM-41(5)-Pre-A	52.0	95.8	60.0	19.1	16.7	4.2
Pt/Al-MCM-41(5)-Pre-N	50.7	94.2	60.8	15.9	17.5	5.8
Pt/Al-MCM-41(5)-Pre-P	54.3	95.7	58.2	26.1	11.4	4.3
Pt/Al-MCM-41(10)-Pre-P	51.3	95.5	56.4	27.1	12.0	4.9
Pt/Al-MCM-41(20)-Pre-P	48.9	92.7	51.0	29.3	12.4	7.3
Pt/Al-MCM-41(40)-Pre-P	47.2	90.0	46.4	30.5	13.0	10.0

Pt/Al-MCM-41(5)-Post	52.5	98.3	72.7	20.9	4.6	1.7
Pt/Al-MCM-41(10)-Post	53.0	95.8	68.9	20.4	6.4	4.2
Pt/Al-MCM-41(20)-Post	54.4	92.6	59.3	25.1	8.2	7.4
Pt/Al-MCM-41(40)-Post	53.1	92.5	59.6	24.8	8.1	7.5

Mono-C_{16} = monobranched isohexadecanes, Di-C_{16} = dibranched isohexadecanes, Tri-C_{16} = tribranched isohexadecanes, B-C_{16} = branched isohexadecanes. *Catalysts have 0.5wt.%Pt content. Reaction at $350^{o}C$, 103 bar.
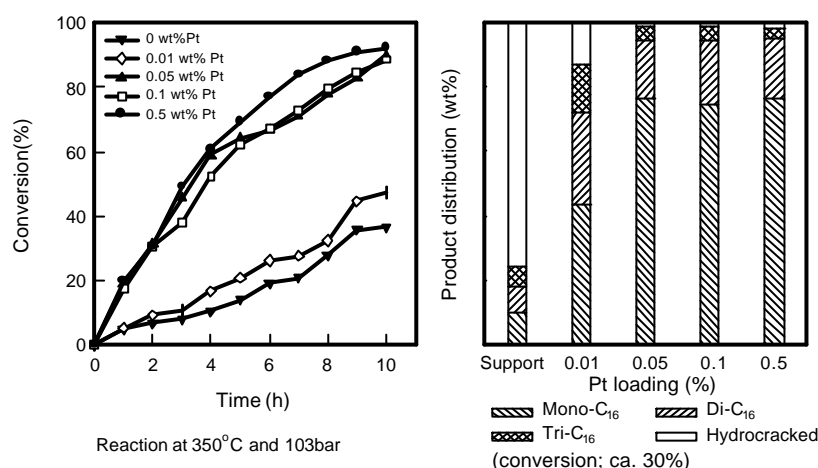

Fig. 6. Temporal conversion and product distribution over Al-MCM-41(5)-Post with Pt loading.

4. CONCLUSIONS

The hydroisomerization of *n*-hexadecane was carried out in a batch reactor at $350^{o}C$ and 103 bar over Pt/Al-MCM-41 bifunctional catalysts, which were reported to be promising candidate for good dewaxing catalysts [1], showing an excellent isomer selectivity (>90%). The catalytic activity decreased in the order of Pt/Al-MCM-41-Post > Pt/Al-MCM-41-Pre-P > Pt/Al-MCM-41-Pre-N > Pt/Al-MCM-41-Pre-A. The higher the acidity of supports was, the higher were the reactivity and isomer yield obtained. The amount of tetrahedral Al sites, potential Broensted acid sites, was larger in Al-MCM-41-Pre than in Al-MCM-41-Post in view of ^{27}Al NMR measurement, while ammonia TPD showed that the amount of acid sites was larger in Al-MCM-41-Post than in Al-MCM-41-Pre. Reaction data did not seem to agree with Al-NMR data but with ammonia TPD. This discrepancy must be due to better accessibility of tetrahedral sites in Al-MCM-41-Post than those in Al-MCM-41-Pre. Platinum loading of 0.05 wt.% could make the conversions to increase drastically, and even small amounts (0.01 wt.%) of Pt loading could change the product distribution from the pattern of cracking to that of hydroisomerization.

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