

Hydroisomerization of n-hexane over Pt–H-MCM-22

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Abstract

Hydroisomerization of n-hexane was carried out at atmospheric pressure in the temperature range 473–573 K over Pt–MCM-22. The influence of Pt content, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the zeolite and the reaction parameters on the isomerization efficiency of the catalyst was investigated. The optimum Pt content for the reaction was found to be around 0.5 wt.%. At a constant Pt content of 0.5 wt.%, increasing the Al content of the zeolite increased the catalytic activities and isomerization/cracking ratios. The studies suggest that the reaction proceeds by a bifunctional mechanism. Preliminary activity comparisons between Pt–H-MCM-22, Pt–H- β and Pt–H-mordenite are reported.

Keywords: Hydroisomerization of n-hexane; n-Hexane hydroisomerization; Pt–H-MCM-22; Zeolites; MCM-22

1. Introduction

Hydroisomerization of light naphtha (C_5 – C_6 fractions) is an industrially important process and is used in the production of high octane gasoline blend stocks [1,2]. The process involves the transformation (with minimal cracking) of the low octane normal (and less branched) paraffin components into the high octane isomers with greater branching of the carbon chain. For example, n-hexane has a blending research octane number (RON) of 19 [3], which on isomerization yields an equilibrium mixture of n- and iso-hexanes, the overall RON of the mixture (at 503 K) being 74.9. As the dimethyl hexanes have larger RON values than the monomethyl pentanes and also constitute a larger propor-

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tion of the equilibrium mixtures at lower temperatures, the development of low temperature isomerization catalysts assumes importance.

Hydroisomerization reactions are generally carried out over bifunctional catalysts, often containing platinum. The metal component aids in increasing the rate of isomerization, besides lowering catalyst deactivation. The reactivity of n-alkanes increases as the carbon number increases but the selectivity towards isomerization decreases [4]. The mono-branched isomers are formed predominantly as they are the primary products. These undergo consecutive reactions to yield multiply branched isomers. The chain length has a marked influence on the reaction rate and on the formation of the multiply branched isomers, which increases on increasing the chain length [4].

The hydroisomerization of n-hexane has already been studied over Pt-loaded zeolites such as Pt-Y [5], Pt-beta (β) [6] and Pt-mordenite (MOR) [7]. There is a general consensus on the mechanism of alkane hydroisomerization. n-alkane molecules are adsorbed at dehydrogenation/hydrogenation sites where n-alkenes are formed. These migrate and interact with acid sites and 2° carbenium ions are generated, which further rearrange to more stable 3° carbenium ions. Finally, the 3° carbenium ions are hydrogenated at the metallic sites yielding isoalkanes [8,9].

MCM-22 is a microporous, high silica zeolite, whose structure was established only recently [10]. It has been claimed to be useful for a variety of hydrocarbon conversion reactions such as alkylation [11], isomerization [12] and cracking [13]. It contains both 10 MR channels and 12 MR cages [10]. It has been reported to exhibit a shape-selective behavior intermediate between medium and large pore zeolites during catalytic reactions [14,15]. In the present paper, we report our studies on the catalytic activity of Pt-loaded H-MCM-22 in the hydroisomerization of n-hexane. A comparison of its performance with those of Pt- β and Pt-mordenite is also being made.

2. Experimental

MCM-22 samples with varying $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios (28, 58, 80) were prepared following previously established procedures [16,17]. The as-synthesized samples were calcined in air at 873 K for 6 h. The as-synthesized and calcined samples were characterized by SEM and XRD. There was no change in crystal morphology on calcination and the XRD patterns were almost similar. The unit cell parameters and adsorption data (Table 1) match the values reported earlier [10]. The slight decrease in the unit cell volume with increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (Table 1) is in the expected direction. The calcined samples were then converted into the catalytically active H^+ -forms by three cation exchanges with ammonium acetate (25 ml of 1M solution/g of zeolite, at 353 K for 8 h), dried at 383 K and calcined at 798 K for 6 h.

Table 1
Physico-chemical properties of the zeolite samples

Zeolite	SiO ₂ /Al ₂ O ₃	S _{BET} (m ² /g)	Sorption, cyclo- hexane (wt.%) ^a	Unit cell parameters (Å)			Unit cell volume (Å) ³
				a	b	c	
MCM-22	28	505	9.5	24.606	14.395	24.753	8767.596
MCM-22	58	447	9.7	24.620	14.343	24.821	8764.907
MCM-22	80	423	10.0	24.635	14.289	24.875	8756.237
Beta (β)	35	600	14.6	–	–	–	–
Mordenite (MOR)	21	592	8.2	–	–	–	–

^a At $p/p_0 = 0.5$ and 298 K.

The H-forms of the samples were exchanged with [Pt(NH₃)₄(NO₃)₂] to achieve Pt loadings of 0.1, 0.2, 0.3, 0.5 and 0.75 wt.%. Pt–H-beta (β) and Pt–H-mordenite were similarly prepared from H-β and H-mordenite samples obtained from PQ, Holland and Norton, USA, respectively. The physicochemical properties of the different zeolites are reported in Table 1.

The catalytic runs were carried out in a down flow fixed bed glass reactor (I.D. = 20 mm). n-hexane was > 99% pure (SD fine-chemicals pvt. Ltd., Bombay). The products were analyzed by gas chromatography (HP 5890) using a capillary column (cross-linked methyl silicone gum, HP1, 50 m × 0.2 mm; detector, FID).

3. Results and discussion

The object of the present study is to examine the usefulness of Pt-MCM-22 as a catalyst for the hydroisomerization of n-hexane. The isomerization of n-hexane over Pt supported on acidic zeolites is believed to proceed by a bifunctional mechanism [7,8]. The metal atoms act as dehydrogenation sites and generate reactive olefinic intermediates. The olefinic intermediates isomerize via carbocations over Brønsted acid sites. The iso-olefins transform into iso-paraffins over the metal atoms by hydrogenation. Studies on the influence of the metal content and the acidity (SiO₂/Al₂O₃ ratio) of the zeolite are important aspects of the overall investigations of bifunctional catalysis.

3.1. Influence of Pt content on n-hexane isomerization

The transformation of n-hexane was carried out at atmospheric pressure in the temperature range of 473 to 573 K over Pt-MCM-22 samples containing different amounts of Pt (0.1 to 0.7 wt.%). All the catalysts deactivated with increasing duration of the run (time on stream = TOS), the deactivation being more rapid during the first few minutes (Fig. 1), the activity becoming reason-

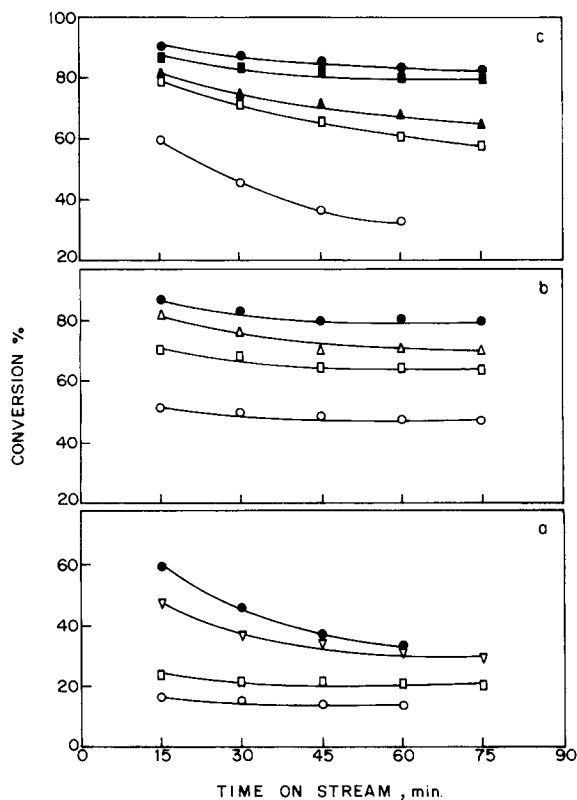


Fig. 1. Effect of temperature and Pt content on catalyst deactivation with duration of the run (time on stream = TOS). (a) Catalyst, Pt (0.1%)–H-MCM-22 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 28$); WHSV (h^{-1}) = 1.0; $\text{H}_2/\text{n-hexane}$ (mole) = 4.5; (○) 473 K; (□) 503 K; (▽) 548 K, (●) 573 K. (b) Catalyst, Pt (0.5%)–H-MCM-22 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 28$); WHSV (h^{-1}) = 1.0; $\text{H}_2/\text{n-hexane}$ (mole) = 4.5; (○) 473 K; (□) 503 K; (△) 548 K, (●) 573 K. (c) Temp. = 573 K; WHSV (h^{-1}) = 1.0; $\text{H}_2/\text{n-hexane}$ (mole) = 4.5; Pt–H-MCM-22 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 28$) with Pt (wt.%): (○) 0.1; (□) 0.2; (▲) 0.3; (■) 0.5; (●) 0.75.

ably stable after 30–45 min. The deactivation rate was also more rapid at higher temperatures, the effect being more pronounced when the Pt content was low (Fig. 1a and 1b). Besides, at a given temperature, the deactivation rate increased with decreasing Pt content (Fig. 1c). Therefore, the data reported in the following sections were mostly collected over catalysts containing 0.5 wt.% Pt and at 503 K at a TOS of 45–60 min. The influence of Pt content ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the zeolite = 28) on conversion at different temperatures is presented in Fig. 2a. The conversion increases with increasing Pt content and reaches a maximum at about 0.5 wt.% Pt. At temperatures above 523 K, the conversion remains constant with a further increase in Pt content but decreases at lower temperatures. The observance of a maximum with Pt loading is typical of bifunctional catalysis [6,8,18]. A similar decrease in the conversion at Pt contents beyond 0.3 wt.% was also observed by Leu et al. [6] during their studies on the isomerization of n-hexane over Pt- β .

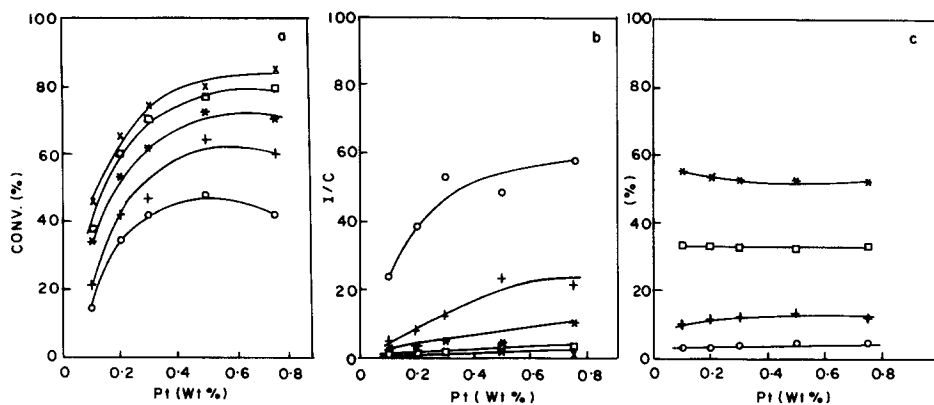


Fig. 2. Influence of Pt content on n-hexane isomerization. Catalyst, Pt (0.5%)–H-MCM-22 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 28$); WHSV (h^{-1}) = 1.0; $\text{H}_2/\text{n-hexane}$ (mole) = 4.5; TOS = 45 min. (a),(b) (○) 473 K; (+) 503 K; (*) 523 K; (□) 548 K; (×) 573 K. (c) Temp. = 503 K; (○) 2,2-DMB; (+) 2,3-DMB, (□) 3-MP; (*) 2-MP.

The influence of Pt content on the isomerization/cracking (I/C) ratios is presented in Fig. 2b. Increasing the Pt content increases the I/C ratio until a plateau is reached at around 0.5 wt.% Pt. Increasing the temperature of the reaction, as expected, decreases the I/C ratios. The Pt content does not appear to influence significantly the C_6 -isomer distribution (Fig. 2c). The 2-methyl pentane/3-methyl pentane (2-MP/3-MP) ratios is ca. 1.63 ± 0.04 at all Pt levels and is close to the equilibrium value of 1.74 expected at the reaction temperature (503 K). However, the dimethyl butanes are not formed in equilibrium amounts. The ratios of the methyl pentanes/dimethyl butanes (MP/DMB ≈ 5.22 –7.19) is larger than the expected equilibrium value of 2.43. Similarly, the 2,3-dimethyl butane/2,2-dimethyl butane ratio (2,3-DMB/2,2-DMB ≈ 2.89 –4.25) is also much larger than the expected equilibrium ratio of 0.59.

3.2. Influence of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio

These studies were carried out at 503 K over Pt-MCM-22 samples containing the same amount of Pt (0.5 wt.%) but different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios. The results are presented in Table 2. The decrease in activity (conversion) with decreasing Al content (increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$) is due to the decrease in available acid sites for the isomerization/cracking reactions. The I/C ratio decreases with increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$.

The interaction between the zeolite and the metal in zeolite supported catalysts has been investigated by many workers [19,20]. The general consensus now is that there is significant electron transfer between the support (zeolite) and the transition metal atoms such as Pd and Pt. Electron enrichment of the metal occurs in alkaline zeolites such as KL [19], while a depletion of electrons occurs in the case of acidic zeolites such as HY [20]. In a given zeolite supported metal

Table 2
Influence of aluminum content of MCM-22 on product distribution ^a

	SiO ₂ /Al ₂ O ₃		
	28	58	80
Product breakup (wt.%)			
C ₁	0.02	0.01	0.01
C ₂	0.07	0.07	0.05
C ₃	1.65	1.35	1.19
i-C ₄	1.19	1.12	1.39
n-C ₄	0.44	0.51	0.44
i-C ₅	0.76	0.82	1.06
n-C ₅	0.24	0.41	0.45
2,2-DMC ₄	2.28	1.72	0.45
2,3-DMC ₄	6.54	5.68	2.16
2-MP	30.07	24.71	18.64
3-MP	18.26	15.45	11.34
n-hexane	38.42	48.12	62.65
C ₆ + aliphatics	0.48	0.05	0.17
2-MP/3-MP ^b	1.65	1.60	1.64
MP/DMB ^c	5.48	5.43	11.49
2,3-DMB/2,2-DMB ^d	2.87	3.30	4.80
I/C ratio	12.90	10.99	6.85

^a Reaction conditions: catalyst = Pt (0.5 wt.%)–H-MCM-22 (SiO₂/Al₂O₃ = 28); temp. = 503 K; WHSV (h⁻¹) = 1.0; TOS (min) = 60; H₂/n-C₆ (mole) = 4.5.

^b Ratio of 2-methyl pentane/3-methyl pentane; equilibrium value = 1.74.

^c Ratio of methyl pentanes/dimethyl butanes; equilibrium value = 2.34.

^d Ratio of 2,3-dimethyl butane/2,2-dimethyl butane; equilibrium value = 0.59.

catalyst, any variation in the acid site content of the zeolite is expected to influence the net electronic property of the metal and hence changes in activity or selectivity for specific products are likely when the SiO₂/Al₂O₃ ratio of the zeolite is changed. Besides, in the case of bifunctional catalysis, where migration of intermediates occurs between the metal and acid sites, the change in the relative densities of the two species could affect selectivities. For example, when the $n_{\text{Pt}}/n_{\text{A}}$ (where n_{Pt} = number of platinum atoms and n_{A} is the number of acid sites) is large, hydrogenolysis due to the metal will be predominant and when $n_{\text{Pt}}/n_{\text{A}}$ is small, acid cracking will be the main reaction. For example, Guisnet et al. [21] have reported that in Pt–H–Y, the hydrogenolysis activity becomes important at $n_{\text{Pt}}/n_{\text{A}} > 0.4$ and the acid activity is important at $n_{\text{Pt}}/n_{\text{A}} < 0.03$. For the given value of $n_{\text{Pt}}/n_{\text{A}} = 0.03$, the cracking selectivity was found to be higher for Pt–H–ZSM-5 than for Pt–H–Y. This was attributed to the greater acid strength of the acid sites and the smaller pore dimensions of H-ZSM-5 slowing the diffusion of the intermediates inside them. The optimum $n_{\text{Pt}}/n_{\text{A}}$ ratio for achieving the maximum I/C ratio, therefore, depends not only on the relative concentration of the exposed metal and the acid sites but also on the strength of the acid sites and pore characteristics.

As discussed above, the decrease in the I/C ratio observed at high

$\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios could be due to an increased hydrogenolysis activity from the 2.9-fold increase in $n_{\text{Pt}}/n_{\text{A}}$ ratio on increasing the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio from 28 to 80. The influence of changes in the electronic state of Pt on changing the $\text{SiO}_2/\text{Al}_2\text{O}_3$ of the support on the I/C ratio is not clear. An increase in hydrogenolysis activity is also suggested by the greater yield of C_4 and C_5 fractions. However, the light product distribution itself is not typical of n-hexane cracking or hydrogenolysis as more (moles of) C_4 and C_5 hydrocarbons are present in the product than can be accounted for by the yields of the C_1 and C_2 fractions. Earlier workers have also reported similar imbalance in product distribution and have attributed it to the occurrence of alkylation–cracking reactions during alkane transformations over metal loaded zeolites [7].

The 2-MP/3-MP ratios are nearly constant (ca. 1.6) over all the samples and are close to the thermodynamic value of 1.74. The MP/DMB ratios and the 2,3-DMB/2,2-DMB ratios increase with decreasing Al content and are larger than the expected equilibrium values. Apparently, though 2-MP/3-MP equilibrium is reached even over the catalyst with the least Al content ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 80$), the other equilibria are not attained even over the catalyst with maximum Al content ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 28$).

3.3. Influence of temperature

The influence of temperature on the reaction is presented in Fig. 3. n-hexane conversion increases with increasing temperature. The increase in conversion is accompanied by an increase in cracking resulting in a decrease of the I/C ratio

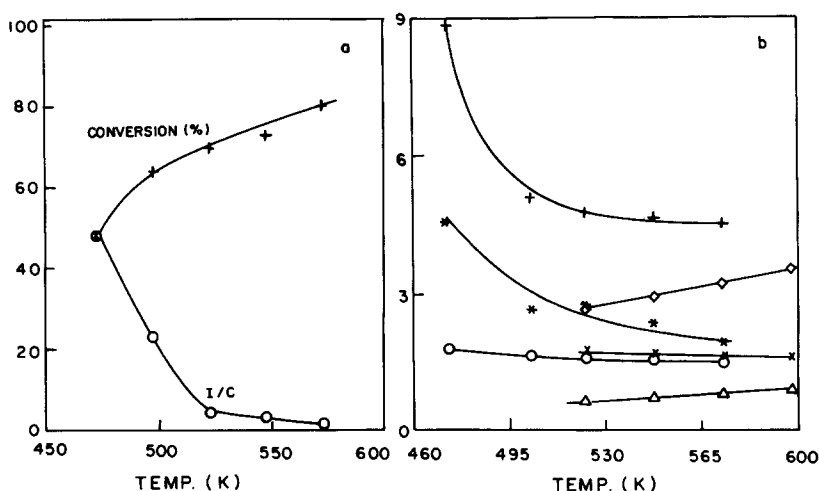


Fig. 3. Influence of temperature on isomerization of n-hexane. Catalyst, Pt (0.5%)–H-MCM-22 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 28$); WHSV (h^{-1}) = 1.0; $\text{H}_2/\text{n-hexane}$ (mole) = 4.5; TOS = 45 min. (b) Isomer ratio (experimental: (○) 2-MP/3-MP; (+) MP/DMB; (*) 2,3-DMB/2,2-DMB; thermodynamic data: (△) 2-MP/3-MP; (◇) MP/DMB; (×) 2,3-DMB/2,2-DMB).

(Fig. 3a). It is likely that the increase in n-hexane fragmentation (cracking) is a result of both increased hydrogenolysis activity of the metal and enhanced cracking over the acidic zeolite. The apparent activation energies (E_a) calculated using extrapolated initial (TOS = 0 min) conversion data in the temperature range 470 to 510 K is 30 kcal mol⁻¹ and is 17 kcal mol⁻¹ based on “steady-state” conversion at TOS = 45 min. The lower E_a value observed at TOS = 45 min is due to the greater activity drop at higher temperatures with duration of the run. The E_a values are similar in magnitude to the values (22–36 kcal mol⁻¹) reported earlier during n-hexane transformation over different samples of Pt-mordenite [9].

The ratios of hexane isomers at different temperatures are presented in Fig. 3b. The 2-MP/3-MP ratios are close to the equilibrium values, but the MP/DMB and 2,3-DMB/2,2-DMB ratios are larger than the equilibrium values. There is, however, a tendency for these ratios to approach the equilibrium values at higher temperatures (Fig. 3b).

3.4. Influence of contact time

Increasing the contact time (1/WHSV) increases conversion and decreases the I/C ratios (Fig. 4a). The decrease in I/C ratios is a result of the increase in cracking reactions, which being slower than the isomerization reactions are favored at higher residence times. The 2-MP/3-MP ratio is ca. 1.63 (at WSHV (h⁻¹) = 0.5), though a slight increase is noticed at the lowest contact time (WHSV (h⁻¹) = 5; 2-MP/3-MP = 1.71, Fig. 4b). A near equilibrium value of 2-MP/3-MP is observed at WSHV (h⁻¹) = 5 even at the low conversion of 23%. The MP/DMB and 2,3-DMB/2,2-DMB values are larger than expected at equilibrium and increase with decreasing contact time (Fig. 4b). Plots of the yield of the hexane isomers at different conversions (Fig. 5) suggest that the methyl pentanes are the primary products of the reaction while 2,3- and 2,2-dimethyl butanes are formed successively from the methyl pentanes.

The ratio of MP/2,3-DMB is 6.14 at WSHV (h⁻¹) = 1 (equilibrium value = 6.54) and increases to 9.97 at WSHV (h⁻¹) = 5. The 2,3-DMB/2,2-DMB ratio is 2.23 at WSHV (h⁻¹) = 0.5 and is far away from the equilibrium value of 0.59. The near attainment of the MP/2,3-DMB equilibrium, the non-attainment of equilibrium between the two dimethyl butanes, and the rapid increase in the 2,3-DMB/2,2-DMB ratio from 2.23 at WSHV (h⁻¹) = 0.5 to 3.44 at WSHV (h⁻¹) = 5, suggest that the transformation of methyl pentanes to 2,3-DMB is faster than the isomerization of 2,3-DMB to 2,2-DMB. The difficulty in transforming a more stable tertiary carbocation (2,3-DMB-carbocation) into a less stable secondary carbocation (2,2-DMB carbocation) is attributed to the slowness in the formation of 2,2-DMB [8]. McCaulay [22] has reported that the relative rates of isomerization of the different hexane isomers over HF/BF₃ are as follows: 2-MP to 3-MP, 58 × 10³; MP to DMB, 58; 2,3-DMB to 2,2-DMB =

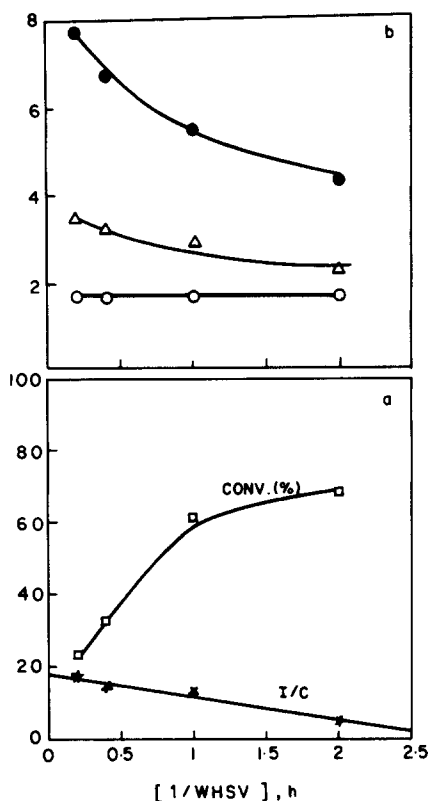
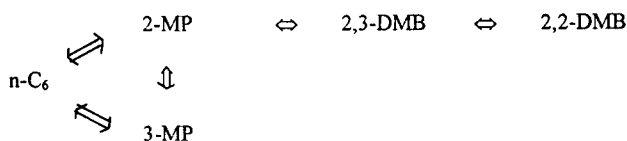


Fig. 4. Influence of contact time on n-hexane isomerization. Catalyst, Pt (0.5%)–H-MCM-22 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 28$); Temp. = 503 K; $\text{H}_2/\text{n-hexane}$ (mole) = 4.5; TOS = 45 min. (b) (○) 2-MP/3-MP; (●) MP/DMB; (△) 2,3-DMB/2,2-DMB.

8.6. Though the relative rates could be different inside the zeolite pores, our studies also point out to similar trends in isomerization rates. Isomerization of 2-MP to 3-MP \gg MP to 2,3-DMB > 2,3-DMB to 2,2-DMB.

The following reaction sequence suggested earlier [8,23] appears to be likely in our case also.



3.5. Influence of $\text{H}_2/\text{n-C}_6$ (mole) ratio

The results of the experiments carried out at different $\text{H}_2/\text{n-C}_6$ (mole) ratios at constant n-hexane feed rate are presented in Table 3. Increasing the partial

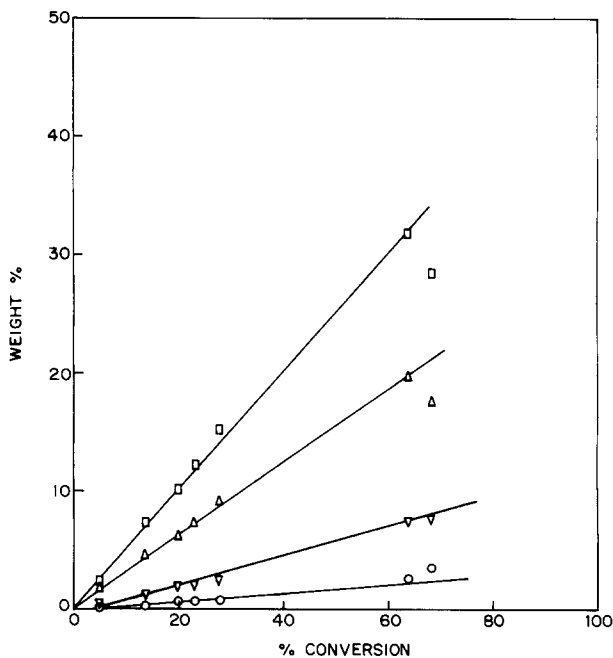


Fig. 5. Distribution of n-hexane isomers in the product at different conversions. Catalyst, Pt (0.5%)–H-MCM-22 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 28$); Temp. = 503 K; $\text{H}_2/\text{n-hexane}$ (mole) = 4.5; TOS = 45 min; WHSV varied; (\square) 2-MP; (\triangle) 3-MP; (∇) 2,3-DMB; (\circ) 2,2-DMB.

pressure of hydrogen from 0.82 to 0.93 ($\text{H}_2/\text{n-hexane}$ (mole) from 4.5 to 15) results in a decrease in conversion and an increase in I/C ratio. A similar increase in I/C ratios with decreasing conversion was also observed during

Table 3
Influence of $\text{H}_2/\text{n-hexane}$ (mole) ratio on product distribution^a

	$\text{H}_2/\text{n-hexane}$ (mole) ratio		
	4.5	10.0	15.0
Conversion (%)	61.58	51.05	46.13
I/C ratio	12.89	17.83	24.84
Products (wt.%)			
$\text{C}_1\text{--C}_5$	7.08	5.17	3.70
2-MP	48.83	48.87	50.10
3-MP	29.65	31.06	32.00
2,3-DMC ₄	10.62	11.20	10.71
2,2-DMC ₄	3.70	3.66	3.32
others	0.11	0.14	0.18
2-MP/3-MP	1.65	1.57	1.57
MP/DMB	5.48	5.37	5.85
2,3-DMB/2,2-DMB	2.87	3.06	3.23

^a Reaction conditions: catalyst = Pt (0.5 wt.%)–H-MCM-22 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 28$); temp. = 503 K, $\text{H}_2/\text{n-C}_6$ (mole) = 4.5; pressure = 0.1 MPa; TOS = 60 min.

contact time studies (Fig. 4). Generally, I/C ratios increase with decreasing conversion as isomerization reactions are faster than cracking reactions. Besides, as cracking of isohexanes is faster than the cracking of n-hexane, cracking reactions are more at high conversions when the isoproducts are present in large amounts. As the studies were conducted at a constant feed rate of n-hexane (WHSV (h^{-1}) = 1), the decrease in conversion could possibly due to the increase in overall ($\text{n-C}_6 + \text{H}_2$) space velocity. Earlier workers have reported reaction orders of 0 to 0.3 with respect to n-C₆ and 0.3 to –0.6 with respect to H₂ for the hydroisomerization of n-C₆ over Pt-mordenite at atmospheric pressure [9]. Therefore, the decrease in conversion at high H₂/n-C₆ ratios could also be due to a negative order with respect to H₂.

The 2-MP/3-MP ratios are close to the equilibrium values at all H₂/n-C₆ ratios studied, while the MP/DMB and DMB ratios are far from the equilibrium values. The ratios deviate more from equilibrium values at higher H₂ partial pressures.

3.6. Comparison of MCM-22 with beta and mordenite

A comparison of the activities of Pt-loaded β ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 35$) and mordenite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 21$) with MCM-22 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 28$) is presented in Table 4. All the zeolites were loaded with the same amount of Pt (0.5 wt.%). The zeolites can be arranged in decreasing order of activities and I/C ratios at constant experimental conditions as: $\beta > \text{MCM-22} > \text{MOR}$. The 2-MP/3-MP ratios are nearly the same (1.57 ± 0.4) being similar to the equilibrium value (1.74) over all the catalysts. The MP/DMB and 2,3-DMB/2,2-DMB values are different over the three zeolites (Table 4), the values being close to the equilibrium values only in the case of MOR. The isohexane distribution observed over MOR, viz., 2-MP : 3-MP : 2,2-DMB : 2,3-DMB = 43.5 : 28.3 : 15.1 : 13.0 is similar to the equilibrium distribution, 44.9 : 25.9 : 18.3 : 10.9. The above distribution is noticed over MOR even when the n-hexane content of the C₆ fraction is 54.3%, while the equilibrium value is 16.9%. The rapid attainment of equilibrium between the isohexanes over mordenite even at a low n-hexane conversion (much less than the equilibrium value) could be attributed to the strong acidity of the Brønsted sites and the slow diffusion of the products through the uni-dimensional pore system. The production of large amounts of the cracked (secondary) products supports the above explanation.

The isomerization of n-hexane rich light naphtha fractions with low octane numbers (RON = 60–70) into octane rich products (RON = 90 +) is already commercially practiced [1,2]. Maximum octane advantage is realized when the feed is converted into an equilibrium mixture of isomers. Hence, the extent to which the equilibrium composition is realized over a catalyst determines its usefulness. We have reported the calculated RON values of the C₆ fraction from

Table 4
Product distribution over different Pt-zeolites ^a

	MCM-22	β	Mordenite	Equilibrium values ^b
C ₆ break up (%)				
n-C ₆	40.20	25.23	54.30	16.9
2-MP	31.46	38.07	19.95	37.4
3-MP	19.11	23.27	12.93	21.5
2,2-DMB	2.39	4.10	6.91	15.2
2,3-DMB	6.84	9.34	5.92	9.0
I/C ratio	12.90	16.89	1.18	–
2-MP/3-MP	1.65	1.64	1.54	1.74
MP/DMB	5.48	4.57	2.56	2.43
2,3-DMB/2,2-DMB	2.87	2.28	0.86	0.59
C ₆ RON ^c	58.88	69.02	49.83	74.91
ATE (%) ^d	71.3	89.9	55.1	–
RON yield ^e	56.3	66.5	35.4	–

^a Reaction conditions: temp. = 503 K; press. = 0.1 MPa; WHSV (h⁻¹) = 1.0; TOS = 60 min; H₂/n-C₆ (mole) = 4.5.

^b Based on Ref. [8].

^c RON of the C₆ fraction calculated from RON values of individual components [3].

^d ATE = approach to equilibrium:

$$\text{ATE} = \frac{\sum C_{ip}(\text{RON})_i - (\text{RON})_{n-C_6}}{\sum C_{ie}(\text{RON})_i - (\text{RON})_{n-C_6}} \times 100,$$

where C_{ip} is the weight fraction of component i in the C₆ fraction of the product, C_{ie} the weight fraction of the component at thermodynamic equilibrium of the C₆ alkanes, $(\text{RON})_i$ the blending octane number of component i and $(\text{RON})_{n-C_6}$ the blending octane number of n-hexane.

^e RON yield = [(C₆ RON) × %C₆ in product]/100.

MCM-22, β and MOR in Table 4 using blending RON values for the individual components [3]. The extent to which equilibrium has been achieved over the different zeolites can be quantified as an approach to equilibrium (ATE) based on the RON of the C₆ fraction in the product and the expected RON at thermodynamic equilibrium of the C₆ alkanes. The method of calculating ATE and the ATE values for the three zeolites is presented in Table 4. β and MCM-22 lead to attractive RON benefits, the ATE being higher (89.9%) over β . It should be noted that ATE can exceed 100% even when an equilibrium of the products is not attained, if the mixture is rich in 2,3-DMB which has the highest blending RON of 96. However, the concept is useful in comparing the abilities of catalysts for RON improvement. Due to its large cracking activity, the RON yield (= RON of the C₆ fraction × weight fraction of the C₆ components in the reaction product) is lowest over MOR. However, it is emphasized that the above zeolites have been compared at common operating parameters which may not be the most suitable conditions for the different zeolites. Besides, the specific β and MOR samples used in this study might not be the optimal ones for the reaction.

4. Conclusions

The studies reveal that the isomerization of n-hexane takes place through a dual functional mechanism over Pt-MCM-22. Both conversion and isomerization/cracking ratio increase with increasing Pt content of the sample and reach a plateau at about 0.5 wt.% Pt. High H₂ partial pressures increase the I/C ratio, while a high Al content increases the conversion and rapid equilibration of the isomers. The octane number (RON) enhancement over Pt-MCM-22 (at 503 K and WHSV (h⁻¹) = 1) is significant.

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