

Nickel Impregnated Pt/H- β and Pt/H-Mordenite Catalysts for Hydroisomerization of n-Hexane

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Abstract—Nickel impregnated Pt/H- β and Pt/H-MOR catalysts with different Ni content were prepared and subjected to hydroisomerization of n-hexane in the presence of flowing H₂ gas. The states of Pt and Ni were identified by ESCA. The particle size measured by TEM shows that average particle size increases with increasing Ni loading. The acidity of the catalysts was measured by TPD of ammonia. The catalytic activity of Ni containing and Ni free Pt/H- β and Pt/H-MOR catalysts was compared and found that addition of Ni up to a threshold value (0.3 wt% for β and 0.1 wt% for MOR) increases the n-hexane conversion and dimethyl butanes selectivity due to better metal-acid synergism and decreases the amount of cracked products. When the Ni amount exceeds the threshold values the conversion decreases and cracked products increase. Further the Ni impregnation of Pt containing acidic supports increases the sustainability of the catalysts and was found to favor the protonated cyclopropane (PCP) intermediate mechanism in n-hexane isomerization. β zeolite was found to be a better potential support than mordenite and the isomerized product mixture shows better octane number.

Key words: n-Hexane, Hydroisomerization, β -Zeolite, Mordenite, Platinum, Nickel

INTRODUCTION

Modern combustion engines require fuels with high research octane number (RON). An environmentally sound way to increase the RON of gasoline is by hydroisomerization of linear alkanes. Weisz and Prater [1954] in their study of skeletal isomerization of n-alkanes on Pt dispersed acidic support (Pt/Al₂O₃) concluded a bi-functional mechanism involving three consecutive steps, namely, dehydrogenation of alkanes, isomerization of the resulting olefin and hydrogenation of the isomerized olefin to iso-alkane. Iglesia et al. [1993] conducted a number of isomerization reactions using n-alkanes over Pt/sulfated zirconia and reported a hydride transfer type mechanism for the reactions. According to their mechanism, hydrogens adsorbed on Pt particles serve as hydride donors and react with the isomerized carbenium ions to form product molecules. Further, they concluded that the hydride transfer is the rate determining step rather than the rearrangement of alkyl carbenium ions, which is in contrast to the Weisz [1954] classical bifunctional mechanism. Tiong Sie [1992] introduced a new type of mechanism from their study of isomerization of n-alkanes over acids, according to which a protonated cyclopropane (PCP) structure forms as intermediate carbenium ion in isomerization and cracking on the acid sites.

Blomsma et al. [1995] in their study on isomerization of n-heptane over Pd impregnated H- β catalysts observed a bimolecular mechanism (C₁₄⁺ intermediate system) leading to more cracked products. Chu et al. [1998] proposed an acid catalyzed chain reaction with the only role of the metal to hydrogenate alkenes in n-hexane isomerization over Pt/H- β . Further they suggested that the metal and

acid sites should be nearer so as to prevent an increase in the local concentration of alkenes. Guisnet et al. [1986] used Pt/H-Y catalysts to isomerize n-heptane and arrived at the conclusion that when the acid sites/metal sites (N_A/N_M) are six and less than six isomerization proceeds without cracking and vice-versa when N_A/N_M is 33 and above. According to Corolleur et al. [1972], isomerization of hexanes is typically structure sensitive for the selectivity; hence the cyclic mechanism is largely predominant on highly metal dispersed catalysts, while the bond shift mechanism is the major one on supported metals of larger size particles. Degnan and Kennedy [1993] concluded in their heptane isomerization over physical mixtures of Pt/Al₂O₃ and zeolite H- β that better synergism exists between metal and acid sites when the ratio of Pt/Al (framework Al) is six. Avery and Anderson [1966] have pointed out that alkane isomerization is accompanied by hydrocracking and the activation energies for the two processes are identical, suggesting that both probably proceed via a common intermediate.

Lee and Rhee [1997] compared the activities of the impregnated catalysts (0.5-2 wt%) Pt/H- β and (0.5-2 wt%) Pt/H-MOR in n-hexane isomerization and found a higher yield of high RON value dimethyl butanes (DMBs) over Pt/H- β than over Pt/H-MOR, because more acid sites are accessible to bulky reaction intermediates in H- β . Blomsma et al. [1997] prepared a series of catalysts by loading β zeolites with Pt, Pd and Pt-Pd combinations via both ion exchange (IE) and incipient wetness impregnation (IWI) techniques and found that bimetallic Pt-Pd zeolites are more active and selective in n-heptane isomerization. Further they reported an improved dispersion of platinum in presence of 20 mole% of Pd (Pt+Pd=100%) and suppression of both undesirable hydrogenolysis and dimerization cracking. The large platinum particles catalyze heptane hydrogenolysis and the lack of intimacy between metal-acid sites favors the dimerization cracking at the acid sites. It is found that the property

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of first dispersed metal is influenced by the addition of second metal due to the formation of bimetallic clusters.

Lugstein et al. [1997] impregnated Ni over H-ZSM-5 and found significantly higher activity in n-heptane hydroconversion compared with free H-ZSM-5 and CoHZSM-5. Rohsclager et al. [1984] reported that nickel-substituted mica montmorillonite shows an enhanced activity in n-hexane isomerization due to Bronsted acid sites of high acidity which is mainly formed during the reduction of octahedrally coordinated lattice nickel. Malyala et al. [2000] compared the activity, selectivity and stability of Ni and Ni-Pt supported Y-zeolite for hydrogenation of acetophenone and found that bimetallic Ni-Pt catalyst was more active and stable on recycle due to strong synergistic effect of Pt in Ni-Pt bimetallic catalysts. Jao et al. [1996] noticed that addition of moderate amount of Ni (0.5 wt%) to Pt (0.26 wt%)/H-MOR catalyst not only suppresses the fuel gas formation but also facilitates the formation of branched isomers in n-hexane and n-heptane isomerization. They suggested that the decrease in fuel gas formation with increasing Ni content of the catalysts is due to the increase in the metallic site/acid site ratio (N_M/N_A). For a catalyst with higher (N_M/N_A) ratio, the diffusion path between two metallic sites is shorter than for a catalyst with fewer metallic sites. They attributed the difference in electronic properties of the Pt particles in Ni-Pt catalyst from those of the Pt catalyst as the cause for the enhanced isomerization activity. Jordao et al. [2000] studied n-hexane isomerization over 1 or 2% of Ni and Pt in different proportions supported on HUSY. It was observed that the bimetallic Ni-Pt catalysts containing 20 to 30% Pt show higher activity and selectivity for high octane dibranched alkanes than Pt only containing catalysts. The higher activity of Ni-Pt catalysts were accounted by i) the presence of Pt enhancing the reduction of Ni cations forming more metal particles, ii) Ni particles serving as support for the Pt atoms and iii) also by higher superficial energy generated due to the interaction between Pt and Ni metal particles.

In the present work Ni was chosen as the second metal to have modified catalytic properties of the Pt dispersed over β -zeolite and mordenite supports and to study the isomerization of n-hexane. Reports on alloy formation between Ni and Pt, along with a common fcc lattice structures are available in the literature [Bertolini et al., 1983]. The purpose of the study involves i) comparison of β and mordenite as acidic supports (with their different pore size arrangements and number of acid sites) loaded with Ni and Pt in low concentrations (0.1 wt% Pt and 0.1 to 0.5 wt% Ni); ii) finding of Ni as to its nature with Pt in the bimetallics as Ni is supposed to suppress hydrogenolysis and cracking similar to Pd in Pt Pd (same group elements); iii) the effect of increasing Ni addition on the ratios of hexane isomers at different temperatures and boosting up of the octane number of the product mixture from n-hexane hydroisomerization.

EXPERIMENTAL

1. Catalysts Preparation

A sample of mordenite was synthesized from gel of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio 12.5 by adopting hydrothermal crystallization method. Water glass, sodium aluminate and tetraethyl ammonium bromide (TEABr) were the sources of Si, Al and template, respectively. The synthesized and dried material was calcined at 550 °C for 8 h to remove

the template molecules. The purity of the crystalline product was confirmed by XRD. The sodium form of zeolite- β ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 10$) was supplied by United Catalyst India Ltd, India. Both β and mordenite samples were converted into ammonium form by repeated ion exchange (3 times) with aqueous solution of 1 M ammonium chloride at 80 °C and then converted into proton forms by calcination at 550 °C for 5 h. H- β was loaded with 0.1 wt% of Pt by incipient wetness impregnation (IWI) technique and the resulting catalyst is designated as A_1 . A part of catalyst A_1 was impregnated with 0.1, 0.3 and 0.5 wt% Ni by IWI method and the resulting materials are designated as A_2 , A_3 and A_4 respectively. Likewise, the acidic support mordenite was impregnated with Pt (0.1 wt%) and designated as catalyst B_1 and B_1 after impregnation with Ni of 0.1, 0.3 and 0.5 wt% resulted in catalysts B_2 , B_3 and B_4 respectively. For comparison purposes, 0.1 wt% Pt 0.3 wt% Ni/H- β and 0.1 wt%Pt 0.1 wt% Ni/H-MOR catalysts prepared by ion exchange (IE) method and are designated as A_5 and B_5 , respectively. Pt loading was done by using aqueous solutions of chloroplatinic acid (Sisco Research Laboratory) (2×10^{-4} g Pt/ml). The chloroplatinic acid is preferred to $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ in the present study as the latter leads to fine Pt particle dispersion in the channels and hence less of skeletal isomerized products in n-hexane isomerization and the former is expected to give coarse particles of Pt outside the pores of supports and hence more skeletal isomerized products. Nickel loading was done by using aqueous solution of nickel nitrate (Central Drug House) of concentration 5×10^{-4} g Ni/ml. The metal loaded catalysts were dried at 120 °C.

2. Characterization

2-1. ESCA

The states of platinum and nickel in the catalysts A_3 , A_4 , B_3 and B_4 reduced at 475 °C for 6-7 h were determined by ESCA. The ESCA spectra were acquired with a surface analysis system (ESCALAB-MKII, VG-Scientific) by using the $\text{MgK}\alpha$ (1253.6 eV) radiation with pass energy of 50 eV. During the spectral acquisition the pressure of the analysis chamber was maintained at better than 1×10^{-7} Torr. All the catalyst samples were insulators with a very small amount of carbonaceous impurity on their surfaces. The charging effect was corrected by setting the C1s transition at 284.6 eV. The catalyst sample powders were placed in a container and were mounted on a sample probe. Calcination and reduction were carried out in the catalyst preparation chamber. So, the catalysts could be moved to the analysis chamber without exposure to air.

2-2. Temperature Programmed Desorption of Ammonia

As the acidic sites at the side pockets are inaccessible in the one dimensional channels of H-MOR to bases like pyridine [Lee and Rhee, 1997] (kinetic diameter 5.85 Å), adsorption of ammonia (kinetic diameter 3.57 Å) was carried out on each of the samples in a quartz tube packed with 0.5 g of the catalyst. The initial flushing out was carried out with dry nitrogen for 3 h followed by reduction in flowing hydrogen (30 ml/min/g) for 6-7 h at 475 °C. Then the system was evacuated (1.5×10^{-5} Torr) at 550 °C for 5 h and cooled to room temperature. Ammonia in vapor form was passed through the catalyst bed repeatedly for saturation of adsorption. The extent of ammonia adsorbed over each catalyst was measured by TGA in a TA3000 Mettler system. Nitrogen as purge gas was passed during the desorption of ammonia. The TGA study was conducted at a heating rate of 10 °C/min up to 650 °C.

2-3. TEM Analysis

Transmission electron microscopy measurements for the catalysts A₃, A₄, B₂ and B₃ reduced at 475 °C for 6-7 h were performed with JEOL200KV electron microscope operating at 200 KV. Catalyst sample powders were dispersed onto "holy carbon" coated grids, which were then introduced to the microscope column, which was evacuated to less than 1×10^{-6} Torr. Specimens were enlarged by using thin photographic paper. The size of the metal particles visible in the photograph is measured manually and the average value is obtained by histogram method.

3. Catalytic Studies

The catalytic reactions were carried out in a fixed bed continuous down flow quartz reactor. 1.5 g of zeolites loaded with metal was packed in the reactor and placed in a tubular furnace. The reaction system was flushed with dry nitrogen for 3 h and then reduced at 475 °C under flowing hydrogen (30 ml/min/g) for 6-7 h. After the reduction process, temperature was lowered to the reaction temperature. n-Hexane was fed into the reactor by a syringe pump at a predetermined flow rate. The LHSV of n-hexane in all the catalytic runs was kept at 1.33 h^{-1} . Pure hydrogen gas (20 ml/min/g) was mixed with n-hexane vapor each time and the reaction was carried out over each catalyst in the temperature range 225-375 °C in steps of 50 °C. The products were collected at ice-cold condition and were analyzed by gas chromatograph (HP 5890) equipped with FID. The identification of products was done by GC-MS (SHIMADZU QP5000). The total yield in the reaction each time was about 95% of the feed. When the reaction was carried out in the reactor without the catalyst, no conversion of the feed was observed indicating that there is no thermal effect on the isomerization reaction.

RESULTS AND DISCUSSION

1. ESCA

The ESCA spectra of Pt and Ni species in reduced form in catalysts A₃, A₄, B₃ and B₄ are shown in Fig. 1. In the case of Pt, two major peaks are observed irrespective of the support and the amount of nickel. The peaks with binding energy values of 71.0 and 74.5 eV are corresponding to the core level Pt4f_{7/2} and Pt4f_{5/2} transitions, respectively, indicating the presence of platinum in metallic state. However, the presence of Pt in higher oxidation state cannot be discarded because of the possibility of overlap with Al2p transition of

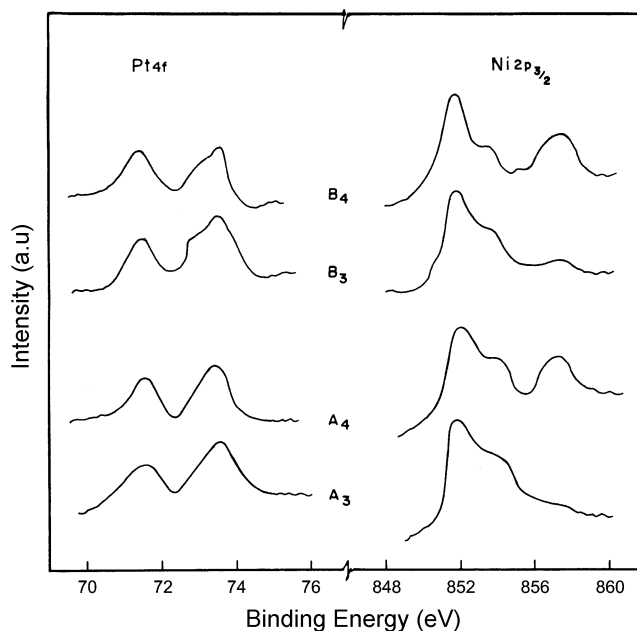


Fig. 1. ESCA spectra of catalysts A₃, A₄, B₃ and B₄.

support. This is similar to the result reported by Arribas et al. [2000] in their XPS study over Pt/ β -zeolite catalyst. The ESCA spectra of Ni2p_{3/2} peaks of all reduced catalysts have two peak maxima with binding energies 852.3 and 854.0 eV indicating the presence of metallic nickel and NiO, respectively. A broad peak seen around 857.0 eV in A₄ and B₄ catalysts indicates the presence of Ni²⁺ and the formation of NiAl₂O₄ from which the reduction of Ni²⁺ is very difficult (Ni metal: 852.3 eV; NiO: 853.3 eV; NiAl₂O₄: 857.2 eV in Phi ESCA data book). The satellite peak some times appearing at 864 eV that is missing in the present XPS spectrum may be due to the very low concentration of NiO. Similar observations were reported by Minchev et al. [1980] in their XPS studies on the reduction of NiY-zeolites wherein they observed remarkable amount of nickel remaining unreduced. The XPS study on Ni-Mordenite by Narayanan et al. [1984] also showed that the reduction of Ni in mordenite is rather difficult and during reduction multiple species of nickel are formed. But Malyala et al. [2000] concluded from their XPS study on Ni/Y-zeolite and Ni-Pt/Y-zeolite catalysts that the addition of Pt causes the reduction of Ni²⁺ to Ni⁰. Thus in the present

Table 1. NH₃-TPD of Pt, Ni-Pt impregnated H- β (A series) and H-MOR (B series) catalysts

Catalyst	SiO ₂ /Al ₂ O ₃	Pt (wt%)	Ni (wt%)	Surface area m ² /g	NH ₃ -TPD mmole/g		Total acidity mmole/g	Particle size (nm) TEM
					LT ^a -Peak	HT ^b -Peak		
A ₁	10	0.1	-	565	0.775	0.189	0.964	nd
A ₂	10	0.1	0.1	527	0.763	0.172	0.935	nd
A ₃	10	0.1	0.3	477	0.710	0.140	0.850	4.55
A ₄	10	0.1	0.5	476	0.575	0.130	0.705	10.78
B ₁	12.5	0.1	-	463	0.728	0.416	1.144	nd
B ₂	12.5	0.1	0.1	405	0.644	0.212	0.856	3.71
B ₃	12.5	0.1	0.3	360	0.634	0.177	0.811	5.42
B ₄	12.5	0.1	0.5	326	0.625	0.172	0.797	nd

^aLow temperature peak, ^bHigh temperature peak, nd-not determined.

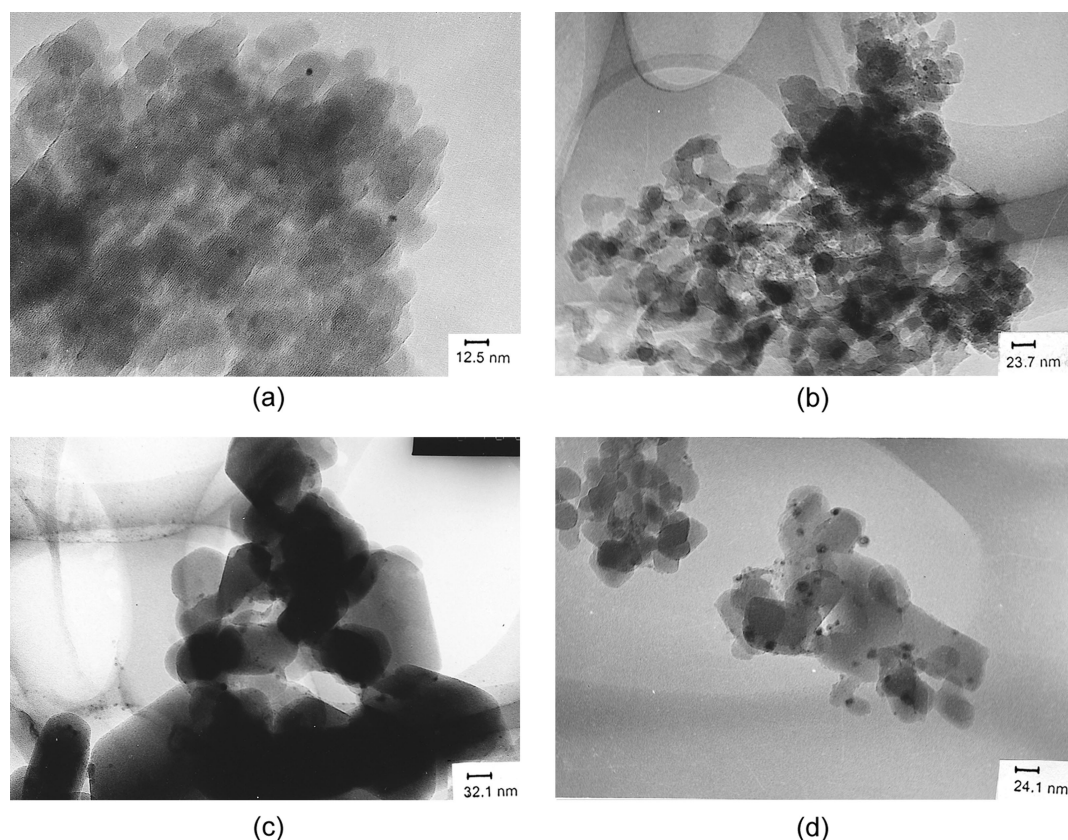


Fig. 2. TEM pictures of catalysts (a) A₃ (b) A₄ (c) B₂ (d) B₃.

case too the added Pt is supposed to favor the reduction of nickel cations in the region 0-0.3 wt% of Ni above which NiO is observed (for 0.5 wt%) in A series catalysts. In B series NiO formation is observed by adding 0.3 wt% Ni itself.

2. Temperature Programmed Desorption of Ammonia

The desorption of ammonia was carried out over A (A₁, A₂, A₃ and A₄) and B (B₁, B₂, B₃ and B₄) series catalysts by TGA method. Table 1 depicts the temperature of desorption and the amount of ammonia desorbed over both series of catalysts. There are two temperature ranges at which desorption occurs. Both A and B series catalysts show their first weight loss in the temperature range 200-250 °C and their second weight loss occur at two different temperature ranges: 350-400 °C (A series) and 500-550 °C (B series). The temperature of desorption and amount of ammonia desorbed, the indexes of strength and number of acid sites, respectively, as Leu et al. [1991] have suggested from their TPD study on Pt/H- β systems, are more in the case of mordenite based Pt, Pt-Ni systems compared to β based Pt, Pt-Ni systems. Jao et al. [1996] reported from their TPD of ammonia study with Pt/MOR and Ni-Pt/MOR systems, a decrease in the number of acid sites with increasing Ni loading and accounted for their observation in terms of occupation of some of the acid sites of mordenite support by nickel species when increasingly loaded. From the decrease in total surface acidity with increase in Ni loading, it is observed that the conclusion of Jao et al. [1996] is again proved. This is further supported by the fact that surface area measured (Table 1) decreases with increasing Ni loading. Further, the decrease in number of acid sites is more pronounced in B series than in A series.

3. TEM Analysis

The TEM picture of catalysts A₃ (maximum activity in A series), A₄ (less active though Ni content is more), B₂ (maximum activity in B series) and B₃ (less active though Ni content is more) revealing the activity changes due to different Ni loadings are shown in Figs. 2a-d, respectively. The average particle sizes determined are presented in Table 1. The particles are supposed to be bimetallic clusters. Jao et al. [1996] in their TPR spectra characterized by a single peak of Ni(0.5) Pt(0.26)/H-MOR observed a decrease in Ni reduction temperature with increasing Pt concentration and presumed a catalytic reduction of Ni due to mobile platinum oxide particles colliding into each other by thermal migration and the nickel oxide particles catalytically reduced by prereduced Pt particles. The average particle (cluster) sizes of catalysts A₃ and B₂ are 4.55 and 3.71 nm, respectively. A₄ and B₃ show an increased average particle size of 10.78 and 5.42 nm, respectively, on increasing the loading of Ni by 0.2 wt%. Such particles may not be smaller in size compared to the pores of β and mordenite and hence are located mainly outside the pores due to thermal mobility as reported by Canizares et al. [1998] in Ni/H-Mordenite catalysts.

4. Catalytic Studies

The product analysis in n-hexane isomerization over A (A₁, A₂, A₃, and A₄) and B (B₁, B₂, B₃, and B₄) series catalysts at 225-375 °C are shown in Tables 2 and 3, respectively. It is invariably found that 2-methyl pentane (2MP), 3-methyl pentane (3MP), 2,3-Dimethyl butane (23DMB) and 2,2-Dimethyl butane (22DMB) are the major products indicating the skeletal rearrangement of n-hexane. Smaller amounts of cracked and cyclized products were also observed irre-

Table 2. Product distribution (wt%) and product ratios in n-hexane hydroisomerization over A series catalystsLHSV=1.33 h⁻¹, H₂ flow rate=20ml/min/g, wt. of catalyst=1.5 g

Products	225°C				275°C				325°C				375°C			
	A ₁	A ₂	A ₃	A ₄	A ₁	A ₂	A ₃	A ₄	A ₁	A ₂	A ₃	A ₄	A ₁	A ₂	A ₃	A ₄
2MP	10.1	12.7	13.5	10.7	20.2	23.4	24.6	19.2	21.3	25.5	25.4	19.0	22.6	25.4	26.5	19.5
3MP	6.0	7.1	8.3	6.0	12.1	13.8	15.5	11.5	13.7	16.0	16.5	12.6	14.6	17.0	17.8	13.7
22DMB	2.0	2.3	3.2	2.2	6.6	8.0	9.0	5.7	8.8	10.2	12.0	9.0	10.5	12.0	14.0	10.8
23DMB	1.0	1.6	2.3	1.5	4.3	5.9	7.3	4.7	6.2	9.0	9.8	7.3	8.3	10.6	12.2	9.2
Crack. Products	1.6	1.5	1.5	2.1	2.4	2.2	2.3	3.1	4.2	4.0	3.8	5.1	4.6	4.5	4.5	5.3
Conversion (wt%)	20.7	25.2	28.8	22.5	45.6	53.3	58.7	44.2	54.4	64.7	67.5	53.0	60.6	69.5	75.0	58.5
MPs/DMBs	5.36	5.07	3.96	4.51	2.96	2.67	2.46	2.95	2.33	2.16	1.92	1.93	1.97	1.87	1.69	1.74
2MP/3MP	1.68	1.78	1.62	1.78	1.66	1.69	1.58	1.66	1.55	1.59	1.53	1.50	1.54	1.49	1.48	1.42
23DMB/22DMB	0.5	0.69	0.71	0.68	0.65	0.73	0.81	0.82	0.70	0.88	0.81	0.81	0.79	0.88	0.87	0.85
2MP/23DMB	10.1	7.9	5.96	7.1	4.7	3.96	3.36	4.08	3.43	2.83	2.59	2.60	2.72	2.39	2.17	2.17
DMBs Selectivity	14.5	15.4	19.0	16.4	23.9	26.0	27.7	23.5	27.5	29.6	32.2	30.7	31.0	32.5	34.9	34.1
I/C	11.9	15.8	18.2	9.7	18.0	23.2	24.5	13.25	11.3	15.17	16.7	9.39	12.17	14.4	15.22	10.0

Table 3. Product distribution (wt%) and product ratios in n-hexane hydroisomerization over B series catalystsLHSV=1.33 h⁻¹, H₂ flow rate=20 ml/min/g, wt. of catalyst=1.5 g

Products	225 °C				275 °C				325 °C				375 °C			
	B ₁	B ₂	B ₃	B ₄	B ₁	B ₂	B ₃	B ₄	B ₁	B ₂	B ₃	B ₄	B ₁	B ₂	B ₃	B ₄
2MP	13.0	15.5	15.0	11.5	16.4	18.0	17.2	15.4	18.3	20.8	20.1	16.0	20.5	22.8	21.3	16.0
3MP	7.5	9.3	8.8	6.3	9.5	11.0	10.1	8.6	11.1	13.6	12.7	9.5	12.5	15.5	15.2	9.0
22DMB	2.5	4.3	3.4	2.0	4.2	6.2	4.8	4.2	7.0	8.6	8.0	5.7	9.5	11.6	8.2	7.2
23DMB	1.3	2.7	2.0	1.0	2.6	4.5	3.0	2.8	4.8	6.3	5.1	3.8	5.7	8.9	6.3	5.5
Crack. products	4.2	4.6	4.8	5.3	5.3	5.0	5.2	5.5	5.8	5.2	5.4	6.0	5.8	5.3	5.5	6.3
Conversion (wt%)	28.5	36.4	34.0	26.1	38.0	44.7	40.3	36.5	47.0	54.5	51.3	41.0	54.0	64.1	56.5	44.0
MPs/DMBs	5.39	3.54	4.4	5.93	3.48	2.71	3.5	3.42	2.49	2.30	2.5	2.68	2.17	1.86	2.51	1.90
2MP/3MP	1.73	1.66	1.7	1.82	1.72	1.63	1.70	1.79	1.64	1.52	1.58	1.68	1.64	1.47	1.40	1.77
23DMB/22DMB	0.52	0.62	0.58	0.5	0.61	0.72	0.62	0.66	0.68	0.73	0.63	0.66	0.6	0.76	0.76	0.76
2MP/23DMB	10.0	5.74	7.5	11.5	6.3	4.0	5.73	5.5	3.81	3.30	3.95	4.21	3.6	2.67	3.3	2.90
DMBs selectivity	13.3	19.2	15.8	11.4	17.8	23.9	19.3	19.1	25.1	27.3	25.5	23.1	28.1	31.9	25.6	28.8
I/C	5.78	6.91	6.08	3.92	6.16	7.94	6.75	5.63	7.10	9.48	8.5	5.8	8.3	11.1	9.27	5.98

spective of the catalysts and conditions of catalytic runs.

From Figs. 3a and 3b, it is observed that nhexane conversion increases with increasing temperature over all the catalytic systems. The effect of Ni addition over Pt/H- β and Pt/H-MOR on n-hexane conversion is studied by comparing the conversion and product selectivities over Ni containing and Ni free catalysts at different reaction temperatures. Thus, when the impregnated Ni is 0.3 wt% over Pt/H- β and 0.1 wt% over Pt/HMOR maximum conversions of n-hexane (75% and 64.1%, respectively) are observed. The number of acid sites in β -zeolite is more than that in mordenite in unit area. However the TPD-NH₃ study shows that the strength of acid sites in β -zeolite is relatively poorer than that of mordenite. For best synergism, conversion and isomerization, the acid sites/metal sites ratio should have a definite bare minimum (normally starts from 6 [from Guisnet et al., 1986]). In the case of β , there is a demand for a greater number of metallic sites, which are finely dispersed Pt-Ni particles due to the addition of second metal, namely Ni. The same type of fine dispersion occurs over mordenite support, where the number of acid sites is less in the main channels and concentrated more

in the side pockets. Thus, the type of synergism that is supposed to exist over β is supposed to exist over mordenite demanding lesser amount of Ni. i.e., 0.1 wt% to disperse Pt into fine particles. Further loading of Ni (>0.3 wt% over β and >0.1 wt% over MOR) results in decreased conversion. The fall in conversion on A₄ in A series and B₃ and B₄ in B series catalysts is attributed to more of unreduced Ni existing as shown by ESCA studies (Fig. 1). Furthermore, the TEM (Figs. 2a-d) analysis shows higher average particle sizes due to increasing Ni loading. This gives the conclusion that more Ni loading above that in A₃ in A series and B₂ in B series results in the formation of bimetallic clusters with Ni partially existing as NiO. The formation of NiO is supposed to cause a decrease in the synergistic effect and hence lesser activity. Thus fall in conversion of n-hexane is realized. Jao et al. [1996] have used Pt Ni/HMOR catalyst system in the conversion of n-hexane and n-heptane and observed a similar trend of fall that occurs after the maximum conversions of 36 and 39.2 wt%, respectively, at 0.5 wt% Ni loading over (0.26 wt%) Pt/H-MOR at 240 °C. The catalysts prepared by ion-exchange (A₅ and B₅) showed considerably lesser activity and

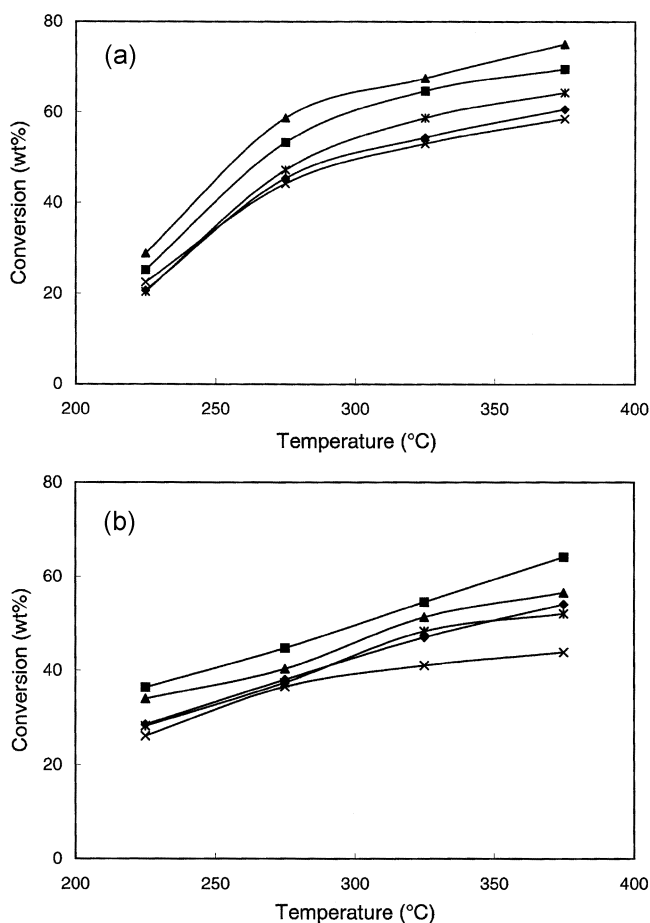


Fig. 3. Conversion (wt%) of n-hexane over:

(a) A series (◆) A₁; (●) A₂; (□) A₃; (×) A₄; (✕) A₅
 (b) B series (◆) B₁; (●) B₂; (□) B₃; (×) B₄; (✕) B₅

isomerization specificity compared to catalysts A₃ and B₂ at all the temperatures studied. A similar observation was made by Chu et al. [1998] in their n-hexane isomerization study over Pt/H-β. They observed that Pt/H-β by IE method gave more cracked products than by IWI method. The maximum activity of the catalysts (A₃ and B₂) as observed in the conversion of n-hexane to isohexanes is supposed to be due to the best metal-acid synergism and the formation of nanoparticles consisting of Pt and Ni as evidenced by TEM analysis. The monomolecular reaction mechanism operates under such synergistic conditions. Thus catalysts A₃ and B₂ are supposed to exhibit best synergism favoring monomolecular mechanism resulting in the maximum skeletal isomerization of n-hexane. It is further observed from Tables 2 and 3 that the cracked products remain under control until the best synergism condition and increases thereafter. The cracking products over the catalyst A₃ and B₂ are minimum and it may be due to the lesser probability for cracking of the olefinic intermediate during the migration from one metallic site to another around the nanoparticle, and hence that would encounter the acidic sites. Similar result was reported by Guisnet et al. [1986] in n-heptane isomerization over Pt/H-Y catalyst in which the cracking rate decreased with the increasing Pt content upto 1 wt% and then became independent of Pt loading.

The effect of temperature on the selectivity of individual iso-

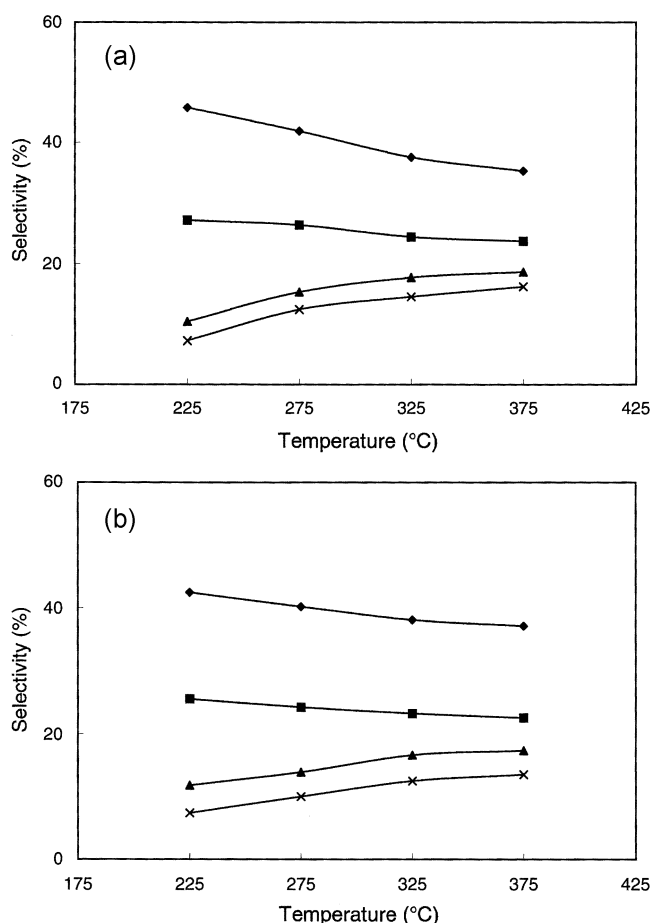


Fig. 4. Effect of temperature on the selectivity of hexane isomers over catalyst (a) A₃; (b) B₂.

(◆) 2MP; (●) 3MP; (□) 2,2-DMB; (×) 2,3-DMB

mers over A₃ and B₂ catalysts is shown in Fig. 4a and 4b, respectively. The selectivity of 2MP and 3MP decreases with increasing temperature over both catalysts. The decrease of 2MP selectivity is much faster with temperature rise. But the selectivity of 2,3-DMB and 2,2-DMB isomers increases over both A₃ and B₂ catalysts. Similar trend is observed over all other A and B series catalysts. The selectivity of methyl pentane isomers (MPs) decreases while the dimethyl butane isomers (DMBs) increases with increasing temperature suggesting the transformation of methyl pentanes to dimethyl butanes.

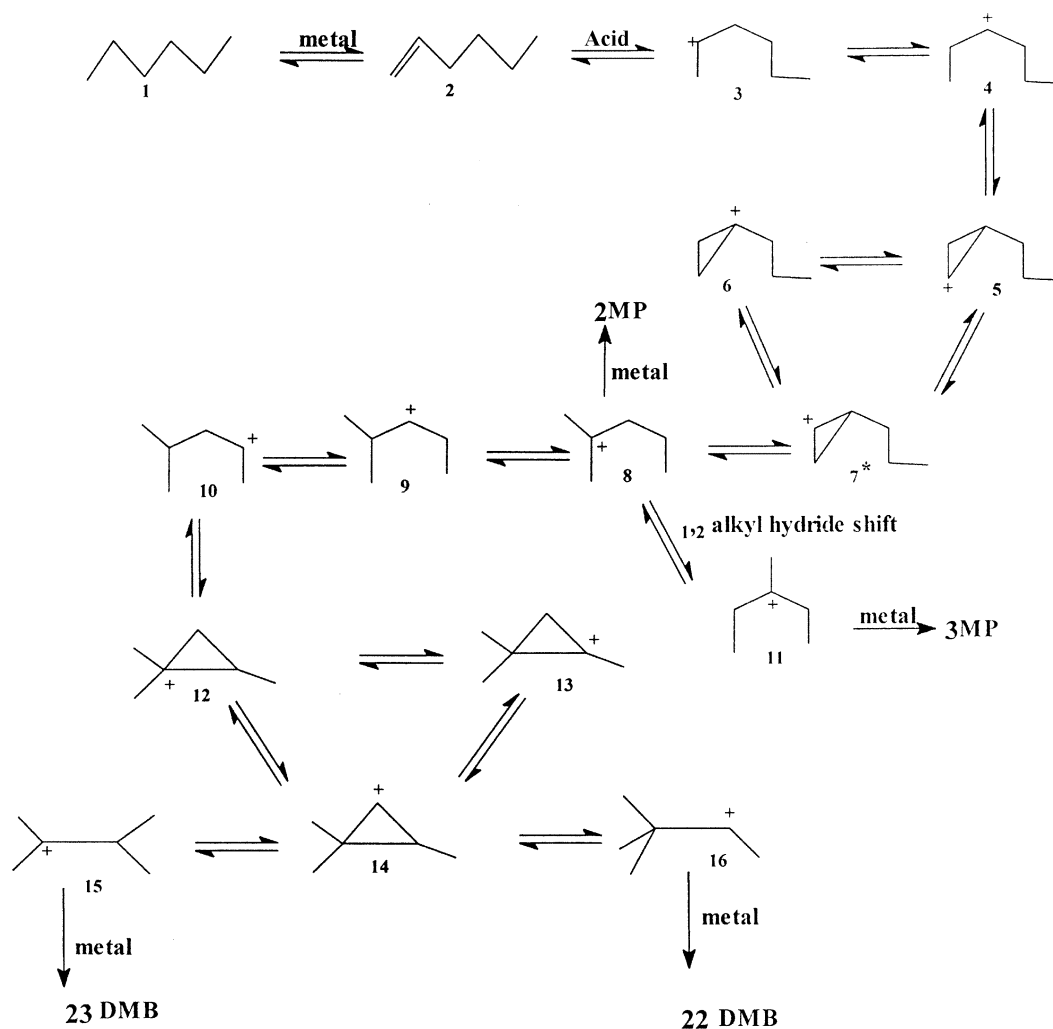
The effect of temperature on the ratios among the isomers of hexane over A and B series catalysts is shown in Tables 2 and 3, respectively. The equilibrium distribution ratios among hexane isomers reported by Condon [1953] and Chen et al. [1988] in their study of n-hexane isomerization over Pt/mordenite catalysts are extended to identify the deviations of the present experimental results. The ratios of MPs/DMBs over both catalytic systems show an opposite trend with respect to the equilibrium ratios which are 2.35 at 225 °C and 4.1 at 375 °C (Condon values [1953]) and 2.6 at 323 K and 3.5 at 598 K (Chen et al. values [1988]) reported. The MPs/DMBs ratio observed over the catalyst A₃ are at 3.96 and 1.69 and the same over B₂ are 3.54 and 1.86 at 225 °C and 375 °C respectively. Thus, when temperature is raised the equilibrium ratio tends towards the thermodynamic ratio. From the free energy consideration of the prod-

ucts and reactants, the equilibrium ratio of MPs/DMBs should be less than unity. The upward deviation of the observed MPs/DMBs ratio at 225 and 375 °C from that of thermodynamic equilibrium ratios (<1) may be due to presence of proportionate kinetic effect on the formation of products. Similar opposing deviations (with respect to Condon and Chen et al. values) in MPs/DMBs ratio were observed for n-hexane isomerization over Pt impregnated SAPO-11 and SAPO-31 by Sivasankar and Sinha [1999]. Thus, it is evident that acidity, pore size and particle size play their role in the ratios of isomers formed at different temperatures.

The increasing addition of Ni upto 0.3 wt% for A series and upto 0.1 wt% for B series system decreases the MPs/DMBs ratio indicating the enhancement of DMBs selectivity by the addition of Ni. Further increase of Ni addition over both catalytic systems shows an increasing trend in MPs/DMBs ratio. The decreasing selectivity of DMBs over catalyst with higher Ni content (A₄, B₃ and B₄) may be due to the hindrance to the movement of DMBs by larger sized (10.78 nm for A₄ and 5.42 nm for B₃ by TEM analysis) bimetallic particles in and outside the pores. The amount of DMBs formed over mordenite catalysts is comparatively low with respect to β based

catalysts even though the acidity of the former is higher than the latter. This is explained in terms of pore structure of the zeolites and kinetic diameter of product molecules. The kinetic diameter of n-hexane is 4.8 Å and that for MPs and DMBs are 5.5 and 6.2 Å, respectively. Mordeinite has one dimensional channels of size 6.7×7.0 Å (12MR) with side pockets (8MR) at the walls of main channels, so that the bimetallic particles grow in size almost to fit the pore size of mordenite channels during the reduction step. Hence acid sites located in the interior to the Ni-Pt nanoparticles in the pores would become inaccessible to the reactants and the intermediates. But zeolite-β consists of intergrowth of linear channels (5.7×7.5 Å) of 12MR and tortuous channel (6.5×5.6 Å) [Higgins et al., 1980] with their intersections. Hence, even if one of the channels is fairly blocked, the reactant and intermediates can have access to metal or acid sites through the other channels.

The 2MP/3MP ratios for catalyst A₃ are at 1.62, 1.58, 1.52 and 1.48 and that from catalyst B₂ lies at 1.66, 1.63, 1.52 and 1.47 at 225, 275, 325 and 375 °C, respectively. These values are close to the thermodynamic equilibrium ratios of 1.70, 1.60, 1.55 and 1.45 at the temperatures mentioned above. The relative formation of 2MP



* detected in GC-MS

Fig. 5. Reaction mechanism for n-hexane isomerization.

to 3MP as per thermodynamic equilibrium ratio indicates that the 1,2-alkyl hydride shift between 8 and 11 of Fig. 5 involved in the interconversion of 2MP and 3MP is extremely rapid [Chen et al., 1988]. The 2,3 DMB/2,2 DMB ratios on catalyst A_3 lie in the range of 0.70 to 0.87 and those from catalyst B_2 lie between 0.62 and 0.68 at 225–375 °C temperature range. These observations show that deviations are on the higher side at low temperature and on lower side at high temperature to thermodynamic equilibrium ratios (0.55 at 225 and to 1.0 at 375 °C). Furthermore, the 2,3DMB/2,2DMB increase is lower to the thermodynamic ratio in the high temperature range over all the catalytic systems. Thus, there may be some inhibition to the formation of 2,2 DMB due to the involvement of a transition from a more stable tertiary 2,3 dimethylbutyl carbocation (15 in Fig. 5) to a less stable secondary 2,2 dimethylbutyl carbocation (16 in Fig. 5) whereas 2,3 DMB is supposed to form from tertiary carbocation (15 in Fig. 5) straightaway. Based on all the above observations and discussions, a tentative mechanism for n-hexane isomerization can be proposed as shown in Fig. 5.

The 2MP/2,3DMB ratio is an indication of the rate of branching of hexane by the protonated cyclopropane mechanism, which is slower than alkyl hydride shift [Chen et al., 1988]. The influence of Ni addition and the ratios of 2MP/2,3DMB at different temperatures are shown in Figs. 6a-b for A and B series catalysts, respectively. From figures it is observed that in A series, the 2MP/2,3DMB ratio decreases (10.10 to 5.96) with increasing Ni addition from 0.1-

0.3 wt% and further increase of Ni increases the ratio (7.1 for A_4) at 225 °C. The same trend is observed in B series where 0.1 wt% Ni addition keeps the ratio low (5.7) and further addition of 0.2 and 0.4 wt% Ni takes the ratio to 7.5 and 11.5 on B_3 and B_4 , respectively, at 225 °C. At higher temperatures corresponding changes are marginal. It is concluded that the addition of moderate amount of Ni (0.2 wt%) in both catalytic system enhances the formation of 2,3DMB through formation of more protonated cyclopropane intermediate 7 and hence 8 in Fig. 5. The formation of cyclopropane intermediate is well supported by the comprehensive rules for carbenium ion rearrangement and cleavage put forth by Brouwer [1980], according to whom the formation of 2,3 DMB proceeds through the precursor of 2MP. The detection of cyclopropane derivative intermediate (7 in Fig. 5) in the GC-MS accounts for the formation of products observed.

It is observed from Tables 2 and 3 that the mere platinum impregnated β and mordenite boosted the selectivity of DMBs to a maximum of 30% during the conversion of about 50%. Under the same reaction conditions, catalyst A_3 and B_2 yield around 35% of DMBs when the extent of conversion is more than 70%. Thus A_3 and B_2 bring about more of conversions without any loss of selectivity of DMBs, which are contributing to the octane number of the resulting product mixture very much. Thus the plots (Figs. 7a-b) of conversion Vs octane number calculated taking account of the oc-

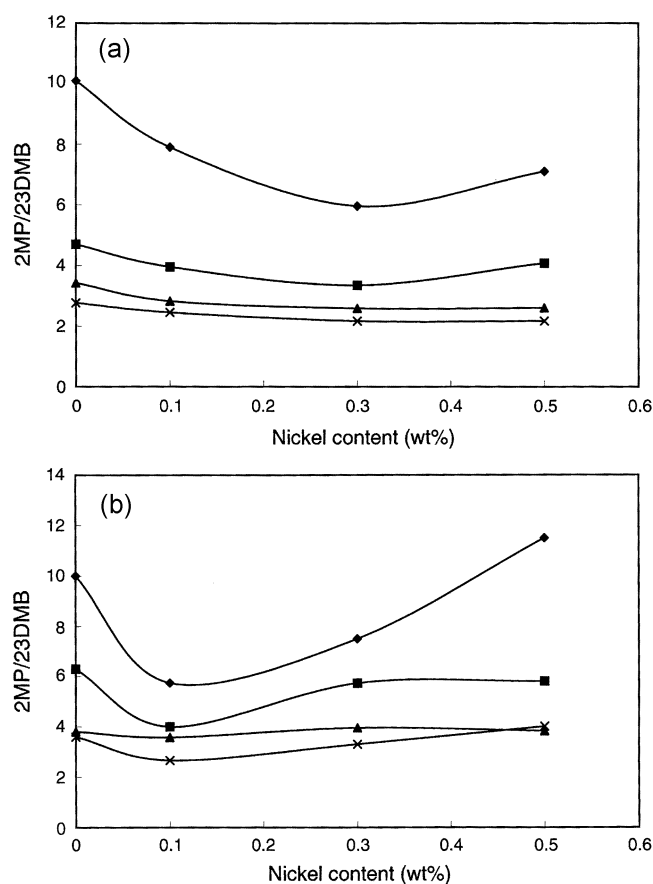


Fig. 6. Effect of Ni addition on the 2MP/23DMB ratio over (a) A series and (b) B series catalysts at different temperatures. (◆) 225 °C; (●) 275 °C; (□) 325 °C; (×) 375 °C

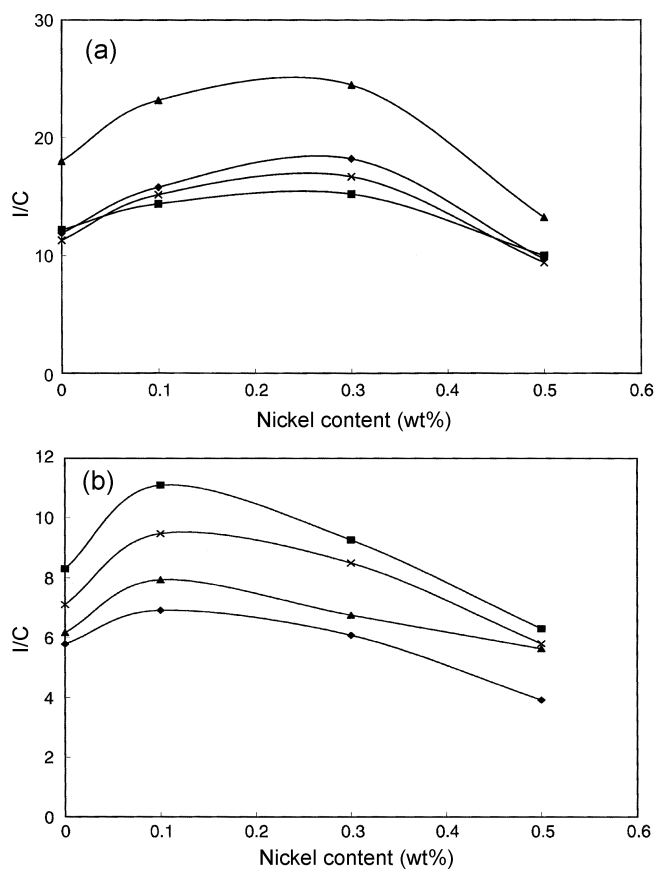


Fig. 7. Plots of octane number of the product mixture Vs n-hexane conversion over.

(a) A series (□) A_1 ; (●) A_2 ; (○) A_3 ; (▲) A_4
(b) B series (□) B_1 ; (●) B_2 ; (○) B_3 ; (▲) B_4

tane number of each individual isomer multiplied by its wt% in the mixture show that catalyst A₃ of A series and B₂ of B series are the ones producing products of well boosted octane number maintaining higher conversion, though A₃ is superior to B₂ on comparison. The higher activity of β -zeolite than mordenite may due to the three-dimensional pore structure, moderate total acidity, higher surface area and higher density of catalytically active acid sites. But mordenite has one dimensional pore structure, and poorer metal-acid balance may due to significant loss of metal sites by isolation in the side pockets of the 8MR and/or pore blockage of the linear 12MR channel. Furthermore, a good measure of the performance of the catalyst for hydroisomerization can be arrived at from the ratios of isomerized products to cracked products (I/C). A better isomerization catalyst yields products with higher I/C ratio at a specified conversion. The effect of Ni addition on I/C ratio of n-hexane isomerization over A and B series catalysts at different temperatures is shown in Figs. 8a-b, respectively. The ratio passes through a maximum (At 0.3 wt% Ni for A and 0.1 wt% Ni for B series catalysts) with

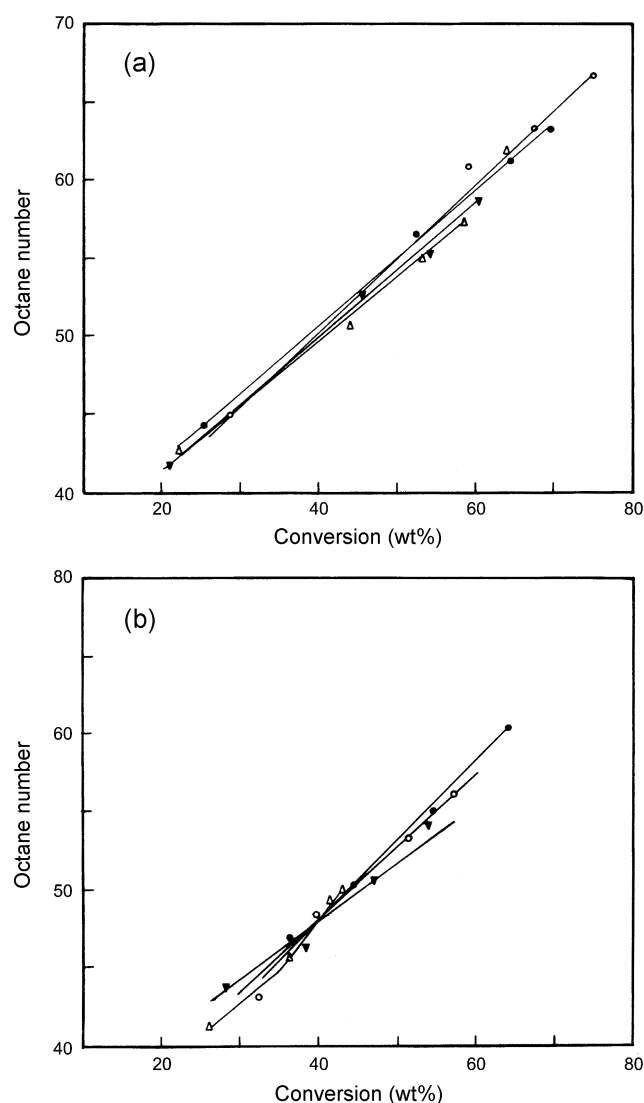


Fig. 8. Effect of Ni addition on the I/C ratio over (a) A series and (b) B series catalysts at different temperatures. (◆) 225 °C; (□) 275 °C; (×) 325 °C; (●) 375 °C

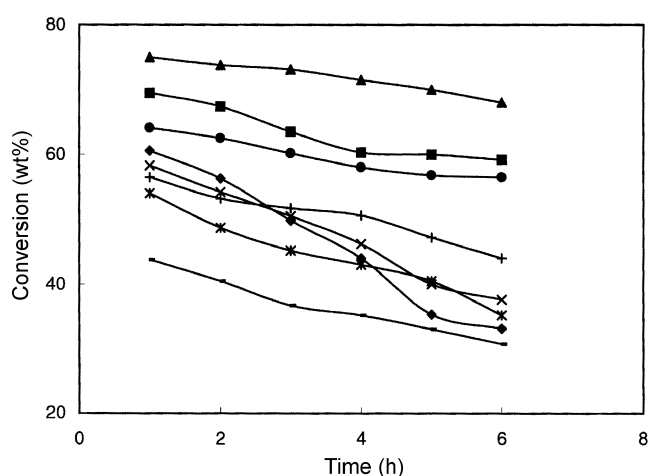


Fig. 9. Time-on-stream behavior of n-hexane hydroisomerization over both A and B series catalysts.

(◆) A₁; (■) A₂; (▲) A₃; (×) A₄; (×) B₁; (●) B₂; (|) B₃; (■) B₄

increasing the nickel addition over both catalytic systems. On A₃ and B₂ the selectivity of cracked products is less due to the better metal-acid balance. At still higher Ni content and temperature, the cracking and hydrogenolysis activity set in due to larger nature of nanoparticles and NiO formation. The amount of cracked products over mordenite based catalysts is higher than that of β based catalysts due to the higher number of acid sites of the former. This conclusion is also depicted in the figure referred above.

The sustainability of activity of these catalysts is studied by conducting a time on stream study for a duration of 6 h (Fig. 9). All the catalysts show high activity during the first one hour and thereafter lose the activity slowly. Catalysts A₃ and B₂ show the minimum fall and A₁ and B₁ show maximum fall in activity among the catalysts studied. This clearly indicates that addition of Ni upto a threshold level to Pt enhances the sustainability. Between A₃ and B₂, again A₃ is superior in showing minimum loss of activity with time.

CONCLUSIONS

The XPS study of Ni-Pt/H- β and Ni-Pt/H-MOR catalysts reveals that Ni exists along with Pt on the support in bimetallic form upto a definite wt% (0.3 wt% over β and 0.1 wt% over mordenite) beyond which NiO forms. From the TEM analysis it has been found that all the bimetallic particles are of nanoparticle size and their size increases with Ni loading. This observation on combination with XPS reveals that catalyst containing 0.5 wt% Ni over 0.1 wt% Pt/ β and that containing 0.3 wt% Ni and above over 0.1 wt% Pt containing mordenite, though having still larger nanoparticles, they do not show expected activity on the basis of Ni loading due to NiO formation. From TPD study β has been found to be possessing lower acidic strength compared to mordenite after the impregnation of Pt and Ni. Because of the best synergistic effect between 0.3 wt% Ni and 0.1 wt% Pt with β -zeolite, it is observed that there is maximum conversion of n-hexane leading to more of MPs and DMBs by protonated cyclopropane intermediate mechanism. Furthermore, the DMBs formed over these catalysts at 375 °C is the main cause for the maximum boost up of the octane number of product mixture. Finally,

the time on stream study gives the conclusion that addition of Ni up to threshold value helps to sustain the activity compared to Ni free Pt impregnated or ion exchanged catalysts.

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REFERENCES

- Anderson, J. R. and Avery, N. R., "The Isomerization of Aliphatic Hydrocarbons over Evaporated Films of Platinum and Palladium," *J. Catal.*, **5**, 446 (1966).
- Aribas, M. A., Marquez, F. and Martinez, A., "Activity, Selectivity, and Sulphur Resistance of Pt/WOx-ZrO₂ and Pt/Beta Catalysts for the Simultaneous Hydrosiomerisation of n-heptane and Hydrogenation of Benzene," *J. Catal.*, **190**, 309 (2000).
- Bertolini, J. C., Tardy, B., Abon, M., Billy, J., Delichere, P. and Marsardier, J., "Surface Reactivity of Platinum-Nickel Single Crystal Alloys: Carbon Monoxide Adsorption," *Surf. Sci.*, **135**, 117 (1983).
- Blomsma, E., Martens, J. A. and Jacobs, P. A., "Isomerization and Hydrocracking of Heptane over Bimetallic Bifunctional PtPd/H-Beta and PtPd/USY Zeolite Catalysts," *J. Catal.*, **165**, 241 (1997).
- Blomsma, E., Martins, J. A. and Jacobs, P. A., "Reaction Mechanisms of Isomerization and Cracking of Heptane on Pd/H-Beta Zeolite," *J. Catal.*, **155**, 141 (1995).
- Brouwer, D. M., "Chemistry and Chemical Engineering of Catalytic Processes," Prins, R. Schult, G. C. A., Eds., Sijthoff and Noordhoff, Germantown, M.D. (1980).
- Canizares, P. de Lucas, A., Dorado, F., Duran, A. and Asencio, I., "Characterisation of Ni and Pd Supported on H-Mordenite Catalysts: Influence of the Metal Loading Method," *Appl. Catal. A: General*, **169**, 137 (1998).
- Chen, J. K., Martin, A. M., Kim, Y. G. and John, V. T., "Competitive Reaction in Intrazeolitic Media," *Ind. Eng. Chem. Res.*, **27**, 401 (1988).
- Chu, H. Y., Rosynek, M. P. and Lunsford, J. H., "Skeletal Isomerization of Hexane over Pt/H-Beta Zeolite: Is the Classical Mechanism Correct?," *J. Catal.*, **178**, 352 (1998).
- Condon, F. E., "Catalytic Isomerization of Hydrocarbons," *Catalysis*, **1**, 6 (1958).
- Corolleur, C., Corolleur, S. and Gault, F. G., "The Mechanism of Hydrogenolysis and Isomerization of Hydrocarbons on Metals. VI. Isomerization of Labeled Hexanes on a 0.2% Platinum-Alumina Catalyst," *J. Catal.*, **24**, 385 (1972).
- Deannan, T. F. and Kennedy, C. R., "Impact of Catalyst Acid/Metal Balance in Hydroisomerization of Normal Paraffins," *AIChE J.*, **39**(4), 607 (1993).
- Glannetto, G. E., Perot, G. E. and Guisnet, M. R., "Hydrosiomerization and Hydrocracking of n-Alkanes. 1. Ideal Hydroisomerisation PtHY Catalysts," *Ind. Eng. Chem. Prod. Res. Dev.*, **25**, 481 (1986).
- Higgins, J. B., Lapierre, R. B., Schlenker, J. L., Rohman A. C. and Wood, J. D., "The Framework Topology of Zeolite Beta," *Zeolite*, **8**, 446 (1988).
- Iglesia, E., Soled, S. L. and Kramer, G. M., "Isomerization of Alkanes on Sulfated Zirconia: Promotion by Pt and by Adamantyl Hydride Transfer Species," *J. Catal.*, **144**, 238 (1993).
- Jao, R. M., Lin, T. B. and Chang, J.-R., "Light Naphtha Isomerization over Mordenite-supported Ni-Pt Catalysts: Effects of Ni on the Catalytic Performance for Pure Feed and Sulphur Containing Feed," *J. Catal.*, **161**, 222 (1996).
- Jordao, H., Simoes, V., Montes, A. and Cardoso, D., "Bifunctional Ni, Pt Zeolite Catalysts for the Isomerization of n-Hexane," *Stud. Surf. Sci. Catal.*, **130**, 2387 (2000).
- Lee, J. K. and Rhee, H.-K., "Characteristics of Pt/H-Beta and Pt/H-Mordenite Catalysts for Isomerization of n-Hexane," *Catal. Today*, **38**, 235 (1997).
- Leu, L.-J., Hov, L.-Y., Kang, B.-C., Li, C., Wu, S.-T. and Wu, J.-C., "Synthesis of Zeolite β and Catalytic Isomerization of n-Hexane over Pt/H- β Catalysts," *Appl. Catal.*, **69**, 49 (1991).
- Lugstein, A., Jentys, A. and Vinek, H., "Hydroconversion of n-Heptane over Co/Ni Containing HZSM-5," *Appl. Catal., A: General*, **152**, 93 (1997).
- Malyala, R. V., Rode, C. V., Arai, M., Hegde, S. G. and Chaudhari, R. V., "Activity, Selectivity and Stability of Ni and Bimetallic Ni-Pt Supported on Zeolite Y Catalysts for Hydrogenation of Acetophenone and its Substituted Derivatives," *Appl. Catal., A: General*, **193**, 71 (2000).
- Minchev, Ch., Knazirev, V., Kosova, L., Pechev, V., Grunsser, W. and Schimidt, F. in L. V.C.Rees (Editor). Proc. 5th Int. Conf. Zeolites, Heyden, London, 335 (1980).
- Narayanan, S., "XPS Studies on the Reduction of Nickel Mordenite," *Zeolite*, **4**(3), 231 (1984).
- Sinha, A. K. and Sivasanker, S., "Hydroisomerisation of n-Hexane over Pt-SAPO-11 and Pt-SAPO_31 Molecular Sieves," *Catal. Today*, **49**, 293 (1999).
- Tiong Sie, S., "Acid Catalysed Cracking of Paraffinic Hydrocarbons. 1. Discussion of Existing Mechanisms and Proposal of a New Mechanism," *Ind. Eng. Chem. Res.*, **31**, 1881 (1992).
- Weisz, P. B. and Prater, C. D., "Interpretation of Measurements in Experimental Catalysis," *Advan. Catal.*, **6**, 413 (1954).