

Blocking of Zeolite Pore by Loading Ni-Pt Nanoparticles for Maximization of Isomerization Selectivity

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Abstract – Zeolite HY is wet impregnated with Ni (0.1, 0.3, 0.4, 0.5 wt%), Pt (0.1 wt%) and reduced in presence of hydrogen to form nanosized particles of Ni and Pt. All the catalysts were characterized by XRD, TEM, ESCA, NH₃-TPD, Pyridine adsorbed FT-IR and BET. Characterization results confirm that the Ni and Pt fractions effectively rehabilitated the physio-chemical properties of the zeolite HY catalysts. Further, all the reduced catalyst were screened with hydroisomerization of *m*-xylene at LHSV = 2.0 h⁻¹ in the temperature range 250-400 °C in steps of 50 °C in hydrogen atmosphere (20 ml/g). The addition of Ni to Pt catalyst increases hydroisomerization conversion, as well as maximizes *p*-xylene selectivity by restricting the pore size. The increasing trend in activity continues up to 0.3 wt% of Ni and 0.1 wt% Pt addition over zeolite HY. The increasing addition of Ni increases the total number of active metallic sites to exposed, which increases the metallic sites/acid sites ratio towards the optimum value for these reactions by better balance of synergic effect for stable activity. The rate of deactivation is pronounced on monometallic catalysts. The results confirm the threshold Ni addition is highly suitable for hydroisomerization reaction for product selectivity over Ni-Pt bimetallic/support catalysts.

Key words: Pore restriction, Ni and Pt nanoparticles, *m*-xylene reaction, Maximization of *p*-xylene selectivity.

1. Introduction

The development of environmentally clean and cost-effective catalytic processes in fine and petrochemical industries has gained importance over the years due to improved environmental awareness. Catalytic processes of petrochemical industries using heterogeneous catalysts have advantageous features of their higher activity, reactant as well as product selectivity, ease of recovery and regeneration/reactivation for economic production. These advantageous features of heterogeneous catalysts also tailor to alter the various factors such as greater surface area, chemical composition, pore/channel size, geometry and distribution of the pores in the catalysts. Zeolites have an edge over the other metal oxides and sulfides because, unlike in the latter, the active sites in the zeolites are well defined and can also be tailored based on the end use application. In addition, they possess high surface area and large adsorption capacity, which can be controlled and varied. The size of the channels with the geometric constraints and intricate channel systems allows them to exhibit shape selectivity, with respect to reactant or product or transition state, in a catalytic reaction [1]. Shape selectivity of the zeolite catalysts has been well documented since it was first described by Weisz and Frilette [2]. In the absence of steric constraints

imposed by the zeolite pores, the same selectivity as with liquid super acid is observed [3]. In particular, zeolites usually show specific selectivity in some reactions due to their microporous properties. It is generally believed that the majority of the active sites are located in the pores of zeolite. The major drawback of monofunctional catalyst is its less activity and selectivity in the transformation involving hydrocarbons such as hydrocracking, hydroisomerization and reforming reactions which require a metal function for hydrogenation/dehydrogenation purposes. Further, due to coke formation during such reactions, the deactivation of monofunctional catalyst is faster. Scientists have introduced “bifunctional catalysts” which are composed of metal/metal ions for hydrogenation/dehydrogenation and acidic supports for acidity. Conventionally, noble metals like Pt, Pd, Re and Rh are loaded over acidic supports like γ -Al₂O₃, SiO₂, clays, zeolites (ZSM-5, Y, β , MOR), aluminophosphate based molecular sieves (SAPO-5, SAPO-11, SAPO-41) and mesoporous materials like MCM-41. Supported Pt, Pd catalysts are well known for their higher activity for hydrogenation, hydrocracking, hydroisomerization and naphtha reforming reactions. The principle behind the use of supported metal catalysts is to increase the effective surface area of metal particles and their dispersion over high surface area support material. In most cases, the metals are loaded by ion-exchange (IE) and incipient wetness impregnation (IWI) techniques.

The present study carried out the hydroisomerization of C₈ hydrocarbons (*m*-xylene) over bimetallic catalysts of Ni-Pt loaded on different zeolite supports. The detailed effects of various physical parameters

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of catalysts compared the chemisorption of *m*-xylene for maximization of *p*-xylene selectivity by blocking of zeolite HY pores with Ni-Pt metallic particles. The parameters included the effect of Ni loading over reaction parameters such as temperature.

2. Experimental Procedures

2-1. Catalytic Materials

Sodium form of zeolite HY with $\text{SiO}_2/\text{Al}_2\text{O}_3=6$ was supplied by United Catalyst India Ltd., India. The surface area of the catalyst is $367 \text{ m}^2/\text{g}$. Chemicals used: Chloroplatinic acid (Sisco Research Laboratory, 38-40% Pt), nickel nitrate (Central Drug House, AR) and demineralized water.

2-2. Preparation of Metal Loaded Catalysts

The sodium form of zeolite HY with $\text{SiO}_2/\text{Al}_2\text{O}_3=6$ was converted into ammonium form by repeated (3 times) ion-exchange with aqueous solution of 1 M ammonium chloride at 80°C and then converted into H-form by calcination at 550°C for 5 h. The H-form of zeolite HY was loaded with 0.1 wt.% Pt by IWI and resulting materials are designated as catalyst Y_1 . A part of catalyst Y_1 was taken each time and was impregnated with 0.1, 0.3, 0.5 wt.% Ni and the resulting samples are designated as Y_2 , Y_3 and Y_4 , respectively, and 0.4 wt.% Ni/H-Y (without Pt) was also prepared by IWI and designated as catalyst Y_6 . For comparison purposes, 0.3Ni 0.1 wt%Pt/H-Y was prepared by ion-exchange method and resulting material designated as catalyst Y_5 . The list of metal loaded zeolite HY catalysts prepared is shown in Table 1.

2-3. Catalyst Pretreatment

Each of the above-mentioned catalysts (1g each) were packed in a quartz reactor and activated at 550°C for 3h under N_2 atmosphere. Then the temperature was lowered to 475°C for Y series catalysts were treated under hydrogen flow (30ml/min) for 6h to reduce the Pt-Ni metal ions.

2-4. Product Analysis and Data Treatment

The total conversion of reactant was determined from the following relationship: Total conversion of reactant (wt.%) = $100 \text{ wt.}\% - \text{wt.}\% \text{ of reactant remaining in the product mixture}$. The product selectivity for individual isomers was obtained from the following relationship:

$$\text{Selectivity (\%)} = N \times 100/X$$

where, N is the wt.% of individual product molecules; X- conversion of the reactant.

2-5. Characterization of Catalysts

2-5-1. X-ray diffraction (XRD)

The phase purity of Ni-Pt loaded zeolite HY samples was analyzed using Rigaku X-ray diffractometer with Ni filter ed $\text{Cu K}\alpha$ radiation ($\lambda = 1.54\text{\AA}$) in the scan range of 2θ between 5 and 60° . The XRD patterns for the Ni-Pt loaded zeolites were analyzed using a Siefert diffractometer with $\text{Cu K}\alpha$ ($\lambda = 1.54\text{\AA}$) radiation.

2-5-2. Transmission electron microscopy (TEM)

Transmission electron microscopy measurements for the reduced catalysts were carried out on a JEOL electron microscope at 200 kV. Catalyst sample powders were dispersed on "holy carbon" coated grids, which were then introduced to the microscope column that was evacuated to less than 1×10^{-6} torr. The size of the metal particles visible in each photograph was measured manually and averaged.

2-5-3. XPS

The state of Ni-Pt metals in the reduced catalysts was determined by XPS. The XPS spectra were acquired with a surface analysis system (ESCALAB-MK11, VG Scientific) by using the $\text{Mg K}\alpha$ radiation (1253.6 eV) with energy of 50 eV. 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 $\text{C } 1s$ transition at 284.6 eV. The catalyst powders were placed in a container and mounted on a sample probe. All the Ni-Pt metal oxide materials were reduced in the same chamber so that the catalyst could be moved to the analysis chamber without being exposed to air. During the spectral acquisition, the pressure of the analysis chamber was maintained at less than 1×10^{-7} torr.

2-5-4. Temperature programmed desorption of ammonia (NH_3 -TPD) and Pyridine Adsorbed FT-IR Spectroscopy

The total acidity of the catalysts was measured by NH_3 -TPD. Adsorption of ammonia was carried on each of the samples in a quartz tube packed with 0.5 g of the catalyst. The initial flushing out was with dry nitrogen for 3h followed by hydrogen (30 ml/min/g) for 6-

Table 1. Physico-Chemical properties of zeolite Y series catalysts

Zeolite HY Catalysts	Pt content (wt.%)	Ni Content (wt.%)	BET Surface Area (m^2/g)	Particle Size by XRD	NH_3 -TPD (mmol/g)		Total acidity (mmol/g)
					LT-peak	HT-peak	
Y_1	0.1	-	340	-	0.423	0.140	0.423
Y_2	0.1	0.1	342	-	0.410	0.124	0.410
Y_3	0.1	0.3	326	5.23	0.386	0.110	0.386
Y_4	0.1	0.5	311	8.3	0.357	0.104	0.357
Y_5^a	0.1	0.3	328	-	0.364	0.117	0.364
Y_6	-	0.4	335	-	0.346	0.126	0.346

^aCatalyst prepared by ion-exchange method; LT- Low temperature; HT- high temperature

7h at 475 °C for Ni-Pt loaded zeolite HY samples. Then the system was evacuated (1.5×10^{-5} torr) at 550 °C for 5 h and cooled to room temperature. Adsorption of ammonia was carried out by passing ammonia vapors over the catalyst bed. After adsorption, the system was evacuated to remove the physisorbed ammonia and again ammonia was passed. The adsorption and evacuation processes were repeated for five times for achieving saturation of adsorption.

The acidity of metal loaded zeolite HY samples was also measured by pyridine adsorbed FT-IR spectroscopy with ammonia as a probe molecule. The pyridine adsorbed catalyst was mixed with KBr (Merck) (1:3), ground and made into thin wafers (pellet) by applying a pressure of about 7×10^3 kg/cm². The thin wafer was placed in FT-IR cell and the spectrum was recorded in absorbance mode with a Nicolet (AVATAR) spectrometer.

2-5-5. BET Surface Area Analysis

Surface area measurements were by Sorptomatic 1990CE Instrument following the BET procedure using N₂ as adsorbent at liquid nitrogen temperature. Prior to adsorption the calcined samples were degassed at 473 K for 15 h. Helium was the carrier gas and TCD was used as detector. The software (Sorptomatic 1990) was used to calculate the surface area from nitrogen adsorption isotherm.

2-5-6. Catalytic Reactor System and Product Analysis

The activity of the prepared catalysts for *m*-xylene hydroisomerization reaction was evaluated at atmospheric pressure in a fixed bed down flow reactor consisting of a quartz tube (8 mm id and 35 cm length) in which ceramic beads was packed in the middle of the reactor to support the catalyst [4]. About 1g of each of the reduced catalyst was packed and placed in the tubular furnace controlled by digital temperature controller. Then the catalyst was activated in N₂ atmosphere at 550 °C for 3 h and the temperature was lowered to reaction temperature. The catalyst was reduced by passing H₂ gas for 5 h. The reactant *m*-xylene was fed into the reactor by a syringe pump at LHSV = 2.0 h⁻¹ and pure hydrogen gas at a flow rate of 20 ml/min was passed with

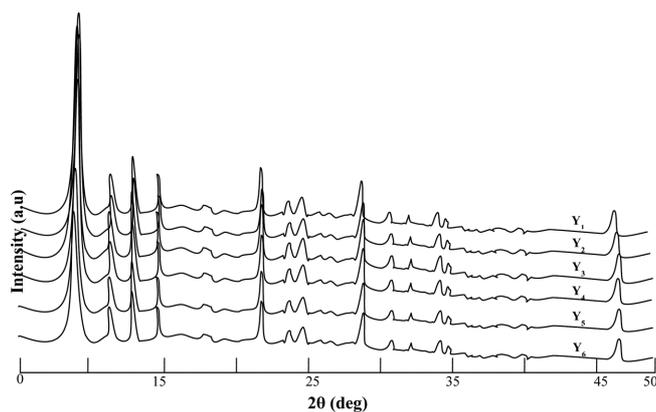


Fig. 1. Line broadening XRD pattern of Bimetallic Zeolite Y catalysts.

reactant. The reaction products were passed through a condenser with circulating ice-cold water, attached to the end of the reactor and were collected in a trap surrounded by ice. The products were analyzed by Hewlett Packard 5890A gas chromatograph equipped with FID and a Bentone column (5% Bentone-34 and 5% diisodecyl phthalate on chromosorb-W) using N₂ as carrier gas. The identification of the products was facilitated by gas chromatography (SHIMADZU QP5000). After each catalytic run the reactor was flushed out with N₂ to remove the adsorbed molecules and the catalyst was regenerated by passing CO₂ free air through the reactor at 550 °C for 5 h.

3. Results and Discussion

3-1. XRD Analysis

XRD patterns of bimetallic zeolite-HY catalysts are in Fig. 1. It is observed that the intensity of the XRD peaks decreases with increasing Ni content over all the catalytic systems. The catalyst-Y₃ with Pt (0.1 wt.%) and Ni (0.3 wt.%) shows high intensity and catalyst-Y₄ with Pt (0.1 wt.%) and Ni (0.5 wt.%) shows low intensity among in bimetallic catalysts. In monometallic catalyst-Y₆ Ni only (0.4 wt.%) shows low intensity pattern. The peaks of Ni (cubic), NiO (hexagonal)

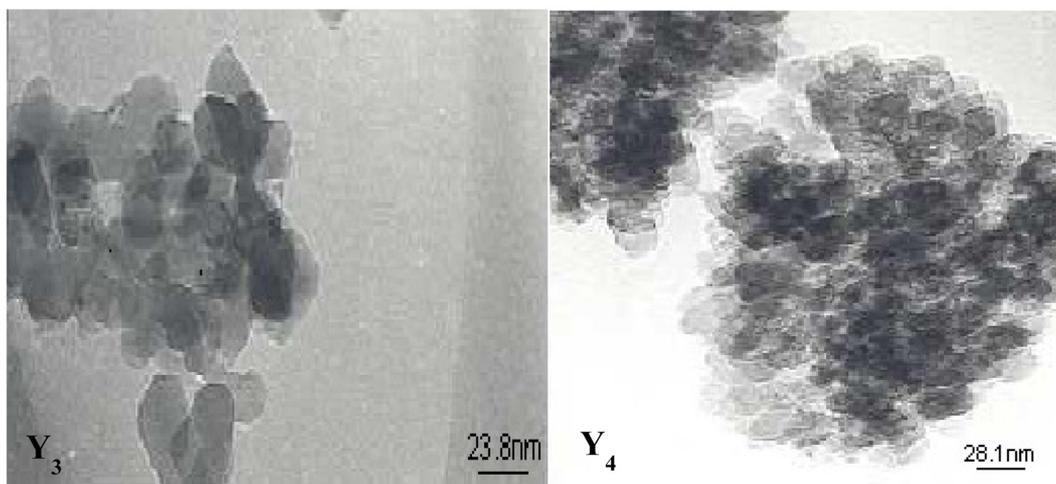


Fig. 2. TEM images of catalysts Y₃ and Y₄ of zeolite Y.

and Pt are expected at the 2θ values of 44.5, 43.3 and 39.8, degrees, respectively. But in the present case, all the above peaks are missing, which may be attributed to low concentration of Pt as well as Ni species. The decrease in the intensity of XRD peaks with increasing Ni addition in all the catalytic systems may be attributed to the decrease in crystallinity. This confirms the presence of Ni-Pt particles over the zeolite HY surface and may increase pore blockage.

3-2. TEM Analysis

The Ni and Pt particles average size on each support is shown in Table 1 and Fig. 2. The addition of Ni-Pt was found to increase the average particle size in all the catalytic systems. The average particle size of catalysts Y_3 and Y_4 was found to be 0.52 nm, 0.83 nm, respectively. Such smaller particles are dispersed over the external surface of zeolite crystal and also inside the channels. A few reports show that large particles are always formed, outside the pores of the zeolite crystal regardless of metal loading technique (ion-exchange and impregnation) [4-7]. TEM analysis shows that the Ni-Pt particle increases with increasing the Ni content on any Pt containing zeolite Y support. For example, in the case of Y_3 , in which the amount of Ni added is 0.3 wt.% over 0.1 wt.% Pt containing samples, it shows 5.23 nm particle size. Further increasing the Ni content to 0.5 wt.% increased the particle size of in Y_4 to 8.3 nm. This increase in the particle size may be attributed to the migration of Ni particles during reduction. The nature of the support does not have much role in the growth of Ni-Pt particles.

3-3. XPS

The XPS spectra of Pt and Ni species in reduced form of catalysts Y_3 and Y_4 of zeolite HY series are shown in Fig. 3. The Pt/zeolite HY series catalysts shows two major peaks irrespective of the support and the amount of nickel. The peaks with binding energy values of 71.0 and 74.5 eV correspond to the core level Pt 4f_{7/2} and Pt 4f_{5/2} transitions, respectively, indicating the presence of platinum in metallic state. Nevertheless, the occurrence of Pt in higher oxidation state cannot be ruled out because of the possibility of overlap with Al 2p transition of the support [8]. The XPS spectra of Ni 2p_{3/2} peaks of zeolite HY series catalysts have two maxima with binding energies of 852.3 and 854.0 eV, respectively, indicating the co-presence of metallic nickel and NiO.

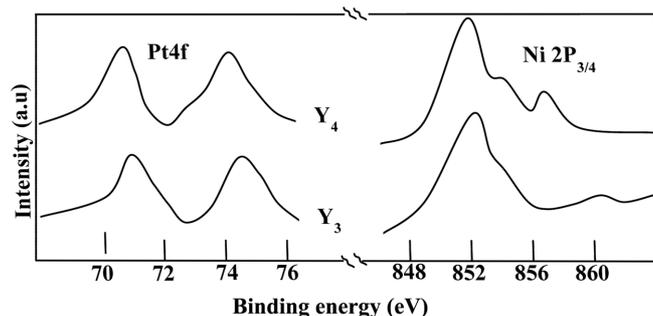


Fig. 3. XPS spectra of catalysts Y_3 and Y_4 of zeolite Y.

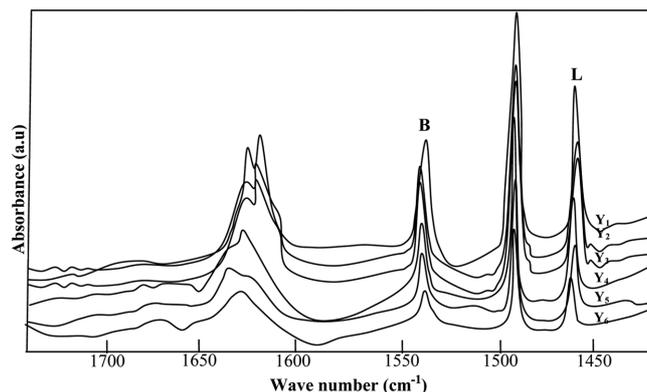


Fig. 4. Pyridine adsorbed FT-IR spectra of zeolite Y series catalysts.

A broad peak seen around 857.0 eV in catalyst zeolite HY_4 indicates the presence of Ni^{2+} and the formation of $NiAl_2O_4$ in which the reduction of Ni^{2+} is very difficult (Ni metal: 852.3 eV; NiO: 853.3 eV; $NiAl_2O_4$: 857.2 eV in XPS data book). The peak appearing at 864 eV is missing in the present XPS spectrum, maybe due to the very low concentration of NiO [9]. But Chaudhari et al. [7] concluded from their XPS study on Ni/Y-zeolite and Ni-Pt/Y-zeolite catalysts that the addition of Pt causes the reduction of Ni^{2+} to Ni^0 . Thus, in the present case the added Pt is supposed to favor the reduction of nickel cation in the region 0-0.3 wt.% Ni. At higher loading of Ni (0.5 wt.%) NiO is observed in zeolite HY series catalysts.

3-4. Pyridine Adsorbed FT-IR Spectra Studies

The pyridine adsorbed FT-IR spectra of zeolite HY series catalysts are shown in Fig. 4. A sharp peak appeared around 1545 cm^{-1} on all the catalysts, indicating the presence of pyridine adsorbed on Brønsted acid sites of zeolites. The pyridine adsorption on Lewis acid sites is indicated by another sharp peak around 1455 cm^{-1} . The increasing addition of Ni in zeolite HY series catalysts has no effect on the position of both Brønsted and Lewis acid site peaks, but the intensity of the each peak was found to decrease, indicating that the number of both Brønsted and Lewis acid sites decreases with increasing Ni loading [10].

3-5. BET-Surface Area Analysis

Table 1 illustrates the surface areas of Ni-Pt loaded zeolite HY series catalysts are measured by BET method. It was observed that the surface areas of catalysts were found to be decreasing with loading of bimetallic (Ni-Pt), irrespective of the amount over the support. Bimetallic samples show the order of $Y_2 > Y_3 > Y_4$ surface area, that clears the amount of metal loading blocks the zeolite HY surface. Whereas, among monometallic Y_1 (Pt only) and Y_6 (Ni only), there was considerably less drop in surface area compared to bimetallic samples. The decrease in surface area with increasing Ni loading can be accounted in terms of the formation of large metal particle size as indicated by TEM. The large particle may block the pores of the support, and hence the surface area of the catalysts decreases.

3-6. Hydroisomerization of *m*-Xylene reaction over Ni-Pt loaded Catalysts

Hydroisomerization of *m*-xylene over metallic catalysts yields isomerization products of *o*- and *p*-xylenes as well as disproportionation products such as 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene and toluene at 250, 300, 350, 400 °C over tubular reactor [4]. The equilibrium product distribution of *o*-, *m*- and *p*-xylene is 24:53:23. The objective of hydroisomerization of *m*-xylene is to achieve maximum conversion of *p*-xylene, as it has high industrial demand for applications compared to *o*-, *m*-xylene. Experimental studies were carried out in order to arrive at the optimum conditions for converting C₈ hydrocarbons into industrially desired product *p*-xylene and to correlate the catalytic activity and selectivity towards *p*-xylene with the physio-chemical characteristics of the prepared catalysts.

3-7. Effect of Ni-Pt Loading over Zeolite-HY

The effect of Ni loading on the conversion of *m*-xylene over Ni-Pt loaded zeolite HY series catalysts was studied in the range 0-0.5 wt.% of Ni on 0.1 wt.% Pt/HY at different temperatures ranges 250 to 400 °C in steps of 50 °C, flow rate of 2.0 h⁻¹. The experimental data obtained in the present study is explained as follows: among monometallic catalyst Y₁ (containing Pt only) was found to be active for the hydroisomerization of *m*-xylene conversion and isomerisation selectivity compared to catalyst Y₆ (containing Ni only) over zeolite HY support. Table 2 data shows that compared to monometallic, bimetallic catalysts do boost the conversion of *m*-xylene and isomerisation selectivity over all the temperatures.

The *m*-xylene conversion increases with increasing reaction temperature over all the catalysts of Ni-Pt loaded zeolite HY series catalysts. The maximum conversion was found at 400 °C, and among all the catalysts Y₃ catalyst showed maximum conversion of *m*-xylene

of 59.1% and 53.4% over Y₂ catalyst. Ni only loaded catalyst-Y₆ showed lowest conversion of 35.2% (Table 2). At all temperatures all the catalysts systems showed both isomerized (*o*-, *p*-xylene) and disproportionate (1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene and toluene) products. Compared to monometallic catalysts, bimetallic catalysts show high yield of isomerization selectivity at all temperatures. High yields of isomerization products due to threshold amounts of loading in zeolite pore selectivity blocked the pore/voids to lead to xylene isomers. The catalyst Y₅ (prepared by ion-exchange method, Table 1) showed enhanced selectivity towards undesired disproportionation products. The effect of Ni addition over zeolite HY catalysts on conversion and isomerization selectivity is shown in Fig. 5 and Fig. 6, respectively. The enhanced disproportionation activity of Y₅ due to decreasing the acidity of 0.364 mmol/g offers considerable restriction to the movements of bulky diphenylbenzenium intermediate, which is cracked and leads to higher disproportionation activity over the zeolite pores. Babu *et al.* [11] studied the transformation of C₈ hydrocarbons over Pt-NiHZSM-5 and perceived that the

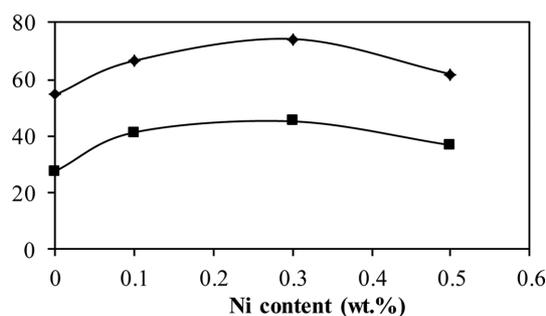


Fig. 5. Effect of Ni addition on *m*-xylene conversion over Y series catalysts at 250 °C: (◆) Isomerization selectivity (*p*-xylene, *o*-xylene) and (■) Conversion (*m*-xylene)

Table 2. Product distribution (wt.%) in *m*-xylene hydroisomerization over Ni-Pt loaded zeolite Y series catalysts

Products (wt.%)	250 °C						300 °C					
	Y ₁	Y ₂	Y ₃	Y ₄	Y ₅	Y ₆	Y ₁	Y ₂	Y ₃	Y ₄	Y ₅	Y ₆
Toluene	3.5	4.9	3.8	4.3	4.0	3.3	3.4	5.2	6.1	4.9	4.2	2.4
<i>p</i> -xylene	7.6	13.8	16.9	11.4	9.8	5.9	7.8	14.3	17.2	12.7	10.1	6.4
<i>o</i> -xylene	7.4	13.6	16.8	11.3	9.7	5.7	8.0	14.4	17.1	12.6	10.0	6.2
1,3,5-TMB	2.8	2.5	2.3	2.9	2.2	2.2	3.4	2.7	3.1	3.2	3.4	3.2
1,2,4-TMB	5.4	5.0	4.1	5.1	5.6	4.4	6.7	6.1	6.2	6.5	6.1	6.3
1,2,3-TMB	1.7	1.4	1.2	1.6	1.5	1.1	2.1	2.1	1.9	2.2	1.8	2.3
Isomerization selectivity	54.5	66.5	74.2	61.8	59.4	52.1	50.3	64.0	66.4	60.0	56.5	47.0
Conversion	28.4	41.2	45.1	36.6	32.8	22.6	31.4	44.8	51.6	42.1	35.6	26.8
	350 °C						400 °C					
Toluene	3.1	7.2	8.1	5.7	4.3	2.5	2.8	5.8	7.2	4.6	3.2	2.3
<i>p</i> -xylene	9.2	15.6	17.7	13.4	10.9	6.8	8.7	14.9	17.5	12.7	11.2	6.8
<i>o</i> -xylene	9.4	15.6	17.4	13.3	11.0	7.0	8.9	14.8	17.3	12.8	11.5	7.0
1,3,5-TMB	4.0	3.6	3.5	3.7	4.3	4.5	5.8	5.1	4.9	5.3	5.7	6.0
1,2,4-TMB	8.9	7.8	7.1	8.5	9.4	8.4	10.3	9.5	9.2	9.8	10.1	10.2
1,2,3-TMB	3.0	2.5	2.3	2.9	2.9	3.2	2.6	3.3	3.0	3.0	3.4	2.9
Isomerization selectivity	49.4	59.5	69.5	62.5	56.2	51.1	42.6	55.0	58.6	45.2	52.9	48.0
Conversion	37.6	52.3	56.1	47.5	42.8	32.4	39.1	53.4	59.1	48.2	43.1	35.2

LHSV = 2.0 h⁻¹, H₂ flow rate = 20ml/min/g, wt. of catalyst = 1g, Time on stream = 1h

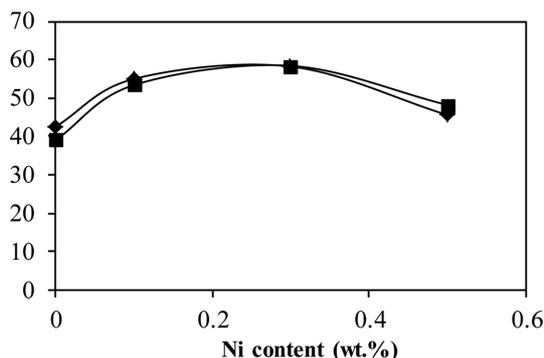


Fig. 6. Effect of Ni addition on *m*-xylene conversion over Y series catalysts at 400 °C: (◆) Isomerization selectivity (*p*-xylene, *o*-xylene) and (■) Conversion (*m*-xylene).

incorporation of nickel and platinum enhances the efficiency of the catalysts in producing *p*-xylene. Simultaneously, these metals suppress the disproportionation and loss of xylenes to toluene and trimethylbenzene.

The conversion efficiency and greater selectivity towards *p*-xylene exhibited in the present study is by the catalyst Y₃. It may be explained on the basis of the average size of the bimetallic particles of Ni-Pt and the effect Ni content on the size of the particles as well as the overall acidity. The average metal particle size in Y₃ and Y₄ was found to be 0.52 nm, 0.83 nm by TEM analysis. Thus, increasing the Ni content in bimetallic catalysts increases the average size of the particles. On the other hand, the total accessible acidity as determined by pyridine adsorption studies decreases with increasing Ni content from 0 to 0.5 wt.%. The larger sized particles of Y₄ catalyst obviously block the pores of the support zeolite HY (pore size=7.4Å), thereby making the acid sites within the pores inaccessible to the reactant molecules and hence a lower conversion. Pore blockage may cause catalyst plugin that leads to deactivation. Boskovic *et al.* [12] compared *n*-hexane isomerization over 0.5 wt.%Pt on NaY catalysts prepared by ion-exchange and impregnation methods and found a lower activity on catalysts prepared by ion-exchange method than impregnation catalysts.

In Y₃ catalyst, the particle size is relatively smaller, allowing the reactant molecules to diffuse through the pores to reach the acid sites to lead desire isomerization selectivity. An optimal amount of total acid sites of 0.386 mmol/g (Table 1) are available in Y₃ catalyst for chemisorption of reaction to form products and easily escape from channels. The maximum activity for the conversion of *m*-xylene observed over catalyst Y₃ is attributed to the better synergic effect from metal-acid sites and is decisive. Jao *et al.* [14] reported that the impregnated Ni increased the metal dispersion over Pt/MOR, and metallic site/acid site ratio is crucial for higher activity. The catalyst prepared by ion-exchange method always showed less activity than impregnation catalysts at all the temperatures studied. Also, greater amounts of dealkylated products were observed over ion-exchange catalysts. Pore size, high surface area, metal and acid strength distribution are the benchmarks of highly active and stable hydroisomerization catalyst.

4. Conclusion

By using the important feature of shape selectivity zeolite catalysts were screened with hydroisomerisation of *m*-xylene to maximize selectivity of isomerization products (*p*-xylene, *o*-xylene) using Ni-Pt bimetallic particles loaded over zeolites-Y. H-form of zeolites were loaded with 0.1 wt.% Pt and varying amounts (0, 0.1, 0.3, and 0.5 wt.%) of Ni using IWI technique for comparison purposes. The metal loaded catalysts were characterized by XRD, XPS, pyridine adsorbed FT-IR spectra and BET-surface area analysis. The average particle size of the bimetallic Pt-Ni particles was measured by XRD. Hydroisomerization of *m*-xylene catalytic activity was screened over all characterized zeolite HY catalytic system. The isomerisation selectivity decreased with increasing reaction temperature and Ni addition above the threshold value. The dealkylation activity is under control up to the threshold Ni content. The following conclusions were drawn: zeolite at threshold value of Ni addition to Pt in low concentration over bimetallic bifunctional catalyst systems shows maximum conversion of hydrocarbon feed (*m*-xylene) with maximum *p*-xylene selectivity at low temperature with good sustainability over time.

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