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Ni–Pt/H–Y zeolite catalysts for disproportionation of toluene and 1,2,4-trimethylbenzene

A. Geetha Bhavani*, D. Karthekayen, A. Sreenivasa Rao, and N. Lingappan

Department of Chemistry, Anna University, Chennai, 600025, India

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Ni–Pt/H–Y zeolite catalysts with different Ni contents were prepared and applied to the disproportionation of toluene and 1,2,4-trimethylbenzene in the temperature range 250–400 °C. The line broadening XRD analysis indicates that the increasing Ni addition decreases the crystallinity of zeolites. ESCA studies show the complete reduction of Ni species up to 0.3 wt.% Ni addition over 0.1 wt.% Pt/H-Y and further addition leads to the occurrence of unreduced nickel species as $NiAl_2O_4$. A TEM study shows the formation of bimetallic (Ni–Pt) particles of nanoscale size and the average particle size is found to increase with increasing Ni loading. Acidity measurements by NH_3-TPD and pyridine-adsorbed FT–IR spectroscopy show the increasing occupation of acid sites by increasing nickel loading. The catalytic activity of Ni–Pt/H–Y zeolite and Pt/H–Y catalysts was compared and it was found that addition of Ni up to 0.3 wt.% increases conversion of toluene and 1,2,4-trimethylbenzene, disproportionation selectivity and sustainability of the catalysts. Further addition of Ni leads to a decrease in conversion and disproportionation selectivity and increasing dealkylated products, which may be due to the presence of unreduced Ni species and pore blockage by large-sized bimetallic particles formed.

KEY WORDS: disproportionation; toluene; 1,2,4-trimethylbenzene; nickel; platinum; zeolite-Y.

1. Introduction

Zeolites and acid catalysts are used for the production of chemicals and intermediates of industrial importance, mainly the alkyl aromatics. The role of zeolites in shape selective catalysis becomes apparent, as only some of the para-isomers are industrially important. Hydroisomerization and hydrocracking are considered hydrogenation-dehydrogenation and Brønsted acid function are widely used [1, 2]. The acid and metal site density and strength distribution are both important and their proper balance is critical in determining the activity of these catalysts [3–5]. It was found that the introduction of second metal influences the property of first dispersed metal due to the formation of metallic clusters [6]. Composite catalysts and metal-supported zeolite have been successfully used to improve toluene disproportionation [7, 8]. Well dispersed metal atoms on acidic zeolites are known to possess electron donor/acceptor properties, to stabilize conversion and suppress coking of hydrocarbons [9]. Jung-chung *et al.* [10] observed that the toluene disproportionation and transalkylation of C_9 aromatics at the temperature range between 370 and 550 °C in presence of H_2 using copper and/or palladium with different wt% by impregnation. They found that the best composition is 8.7 wt% Cu and 0.69 wt% Pd supported mordenite respectively, with conversion of 53%. Dimitrova *et al.* [11] studied the conversion of toluene over CaY, RECaY, Pt/RECaY. Thus the inclusion of platinum catalysts a metal zeolite system is obtained after reduction and it is possible that some different type of active sites may participate in the catalysts. Kikuchi *et al.* [12] introduced the trimethylbenzene (TMB) over montmorillonite intercalated by zirconium oxide and compared with zeolite H–Y and observed that 1,2,4,5-tetramethylbenzene (TeMB) and *o*-xylene were the main products. Se–Ho Part *et al.* [13] investigated the conversion of 1,2,4-TMB over zeolite NU-87 and observed that disproportionation products (xylene) are in thermodynamically controlled within the micropores, while the isomerization to 1,2,3 and 1,3,5-TMB isomers occurs largely on the external surface, whereas in the case of TeMB isomers, 1,2,4,5-isomer is selectively formed inside the pores. Roger *et al.* [14] studied the conversion of 1,2,4-TMB over HZSM-5 at 450°C. They observed the conversion levels below 10% and the isomer distributions in the xylene and TeMB fraction are not thermodynamically controlled. Jao *et al.* [15] studied *n*-hexane and *n*-heptane isomerization over 0.2 wt% Pt and varying amounts (0, 0.26, 0.5 and 1.5 wt%) of Ni on H-mordenite. They observed that the addition of Ni up to 0.5 wt% not only enhances the conversion and rate of branched isomer formation but also suppresses fuel gas formation. Malyala *et al.* [16] compared Ni and Ni–Pt supported on Y-zeolite for acetophenone hydrogenation and found that Ni–Pt/Y–zeolite was more active, selective and stable than Ni/H–Y zeolite catalysts. Further they concluded that a strong synergistic effect of Pt in the Ni–Pt bimetallic catalysts is responsible for the higher

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* To whom correspondence should be addressed.
E-mail: gitabhavani_19@yahoo.co.in

activity observed. Jordao *et al.* [17] studied 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) the Ni particles serving as support for the Pt atoms and (iii) the generation of higher superficial energy due to difficulty in accommodation of Pt atoms in Ni metal particles. The enhanced activity was accounted in terms of better metal–acid balance between catalytically active bimetallic (Ni–Pt) nanoparticles formed and acid sites of the support. Catalysts with higher Ni content show poor activity due to pore blockage by larger bimetallic particles formed and incomplete reduction of nickel species. Dominguez *et al.* [18] reported alloy formation between Ni–Pt with a common fcc lattice structure suggesting some potential bimetallic interactions between these two metals and hence allowing for the catalytic active in hydrocarbon reforming reactions.

Some reports are available in literature where Ni and Pt were used as bimetallic system, but they used in higher concentrations i.e. greater than 0.5%. In the present study, nickel is introduced as the second metal in low concentration (<0.5 wt%) to modify the catalytic properties of Pt supported zeolites-Y (with different acidic properties as well as pore size arrangements) on toluene and 1,2,4-TMB disproportionation. Further results are correlated with amount of metal loading, reaction temperature and acidity of catalyst.

2. Experimental

2.1. Catalyst preparation

The sodium form of zeolite-Y ($SiO_2/Al_2O_3 = 6$) was supplied by United Catalyst India Ltd., India. H–Y was obtained by repeated ion exchange with aqueous 1 M NH_4Cl solution followed by calcination at 550 °C for 5 h. A part of H–Y was loaded with 0.1 wt% Pt by incipient wetness impregnation (IWI) and the resulting materials are designated as catalyst C_1. Part of catalyst C_1 was separately impregnated by IWI method with 0.1, 0.3 and 0.5 wt% Ni and the resulting samples are designated as C_2, C_3 and C_4 (C series) respectively. For comparison purposes 0.3 wt% Ni, 0.1 wt% Pt/H–Y was prepared by ion-exchange method (IE) and the resulting material is designated as catalyst C_5. Catalysts 0.4 wt% Ni/H–Y was also prepared by IWI and is designated as catalyst C_6. Aqueous solution of chloroplatinic acid (E-Merck; 2×10^{-4} g Pt/ml) and nickel nitrate (Central Drug House; 5×10^{-4} g Ni/ml) were used as sources for Pt and Ni, respectively. The metal loaded catalysts were dried at 120 °C for 12 h. Each of the earlier mentioned catalysts (1 g each) were packed in a quartz reactor and activated.

2.2. Characterization

The dried metal-loaded catalysts were activated at 550 °C for 3 h under N_2 atmosphere and lowered to 475 °C and maintained under hydrogen flow (30 ml/min/g) for 6 h in order to reduce the metal ions. The reduced catalysts were used for further characterization as well as for catalytic studies. The line broadening XRD pattern for the metal loaded zeolites were analyzed using a Siefert diffractometer using CuKα radiation ($\lambda = 1.54$Å). The state of metals in the reduced catalysts C_3 and C_4 were determined by ESCA. The ESCA spectra were acquired with a surface analysis system (ESCALAB-MK11, VG Scientific) by using the MgKα radiation (1253.6 eV) with 50 eV of energy. Transmission electron microscopy measurements for catalysts C_3 and C_4 were carried out in JEOL 200 kV electron microscopic at 200 kv. Catalyst sample powder was dispersed on to "holy carbon" coated grids, which was then introduced to the microscope column at 1×10^{-6} Torr. Specimens were enlarged using thin photographic paper. The size of the metal particles visible in each photograph was measured manually and averaged.

The total acidity of the catalysts was measured by TPD of ammonia by a TGA method following the experimental procedure reported in our group studies [19]. Instead of ammonia, adsorption was carried out with pyridine vapor and the FTIR spectra were recoded for catalysts C_1, C_3 and C_4 using KBr pellet technique [19] in absorbance mode with a Nicolet (AVATAR) spectrometer. Surface area measurements were carried out in sorptomatic 1990 CE Instrument following the BET procedure using N_2 as adsorbent at liquid nitrogen temperature.

2.3. Catalytic studies

The toluene and 1,2,4-TMB disproportionation were carried out at atmospheric pressure in a fixed bed continuous down flow quartz reactor. About 1 g of catalyst was packed and placed in a tubular furnace. The reactor system was flushed with dry nitrogen for 3 h and then the metals were reduced at 475 °C under hydrogen flow (30 ml/min/g) for 6 h. After reduction, the temperature was lowered to reaction temperature. The reactant 1,2,4-TMB was fed into the reactor by a syringe pump at LSHV = 1.33 h^{-1}, along with pure hydrogen gas at a flow of 20 ml/min/g. The reaction products were passed through condenser in ice cold condition attached to the end of the reactor and were collected after 1 h in receiver flask. The products were analyzed by Hewlett Packard 5890A gas chromatograph equipped with FID. The identification of the products was done by GC-MS (SHIMADZUQP5000).

2.4. Mass balance studies for coke formation

The formation of coke on the catalyst due to the effect of time-on-stream was studied by mass balance technique. The studies were carried out using 1 g of C_3 catalyst at 350 °C and LHSV 1.33 h^{-1}. To determine the amount of coke formed during reaction the time-on-stream studies were conducted for 5 h. In this study the catalysts and reactant were weighed before and after the experiment. The difference between the weights obtained at the end gave the net weight loss.

The catalysts are subjected to calcination at 500 °C after the reaction for a period of 5 h and then cooled to room temperature and weighed .The difference between the weight of the catalysts before and after calcinations is the weight of the coke.

3. Results and discussion

3.1. Characterization

3.1.1. XRD

The XRD pattern (not shown) of zeolite-Y exhibits the most intense diffraction peaks at 2θ =2–25°, thus confirms the structure of FAU as well as good crystalline nature and found to be in good agreement with standard reference [20].

3.1.2. Line broadening XRD

Line broadening XRD patterns obtained for catalysts C_3 and C_4 are shown in figure 1. The intensity of the XRD peaks is found to decrease with increasing Ni addition in the system. By using CuKα X-ray, the intense peaks of Pt, Ni (cubic) and NiO (hexagonal) are expected at the 2θ values of 39.8, 44.5 and 43.3°, respectively. But in the present case, all the above peaks are missing may be due to lower concentration of Pt as well as Ni species. The decrease in XRD peak intensity with increasing Ni addition over the system can be increasing pore blockage of support materials by the added Ni species.

3.1.3. TEM analysis

The TEM pictures of catalysts C_3 and C_4 are in shown figure 2(a) and (b), respectively. The black dots seen on the support matrix are bimetallic (Ni–Pt) particles on the surface of the supports. The average size of the particles on each support is determined and is presented in Table 1. It is observed that the average particle size is found to increase with increasing Ni addition. Similar observations were already made in our previous studies over Ni–Pt loaded zeolites [21, 22]. The average particle sizes of catalysts C_3 and C_4 are found to be 5.23 and 8.3 nm, respectively. Such particles may be larger in size compared to the pores of zeolite supports with a chance for thermal mobility during reduction and hence may be located mainly outside the pores as reported by Canizares *et al.* [23]. Ostard *et al.* [24] analyzed the TEM pictures of 0.9 and 5 wt% Pt containing MOR and found that the average Pt particle size increases with increasing metal content as well as increasing metal reduction temperature. From the current observation Ni–Pt particle of definite size grows further on the addition of Ni, and this is may be due to migration of Ni particles during the reduction.

3.1.4. ESCA

The ESCA spectra of Pt and Ni species in reduced catalysts C_3 and C_4 are shown in figure 3. 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 Pt $4f_{7/2}$ and Pt $4f_{5/2}$ transitions respectively indicating the presence of platinum in metallic state [21]. However the presence of Pt in higher oxidation state can not be discarded because of the

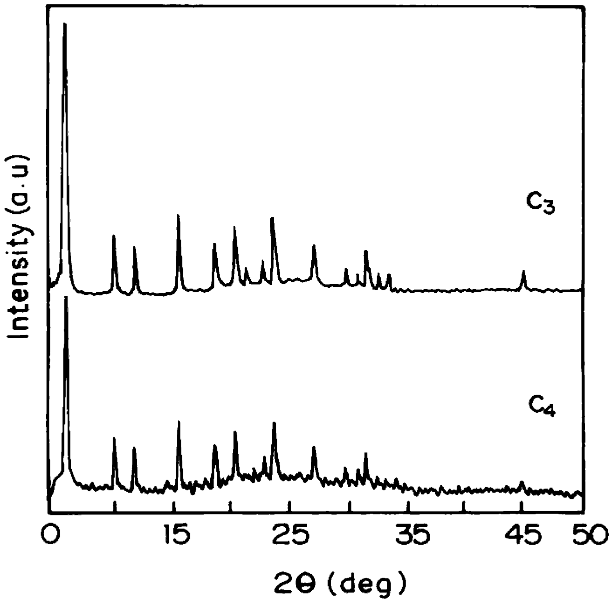

Figure 1. Line broadening XRD patterns of catalysts C_3 and C_4.

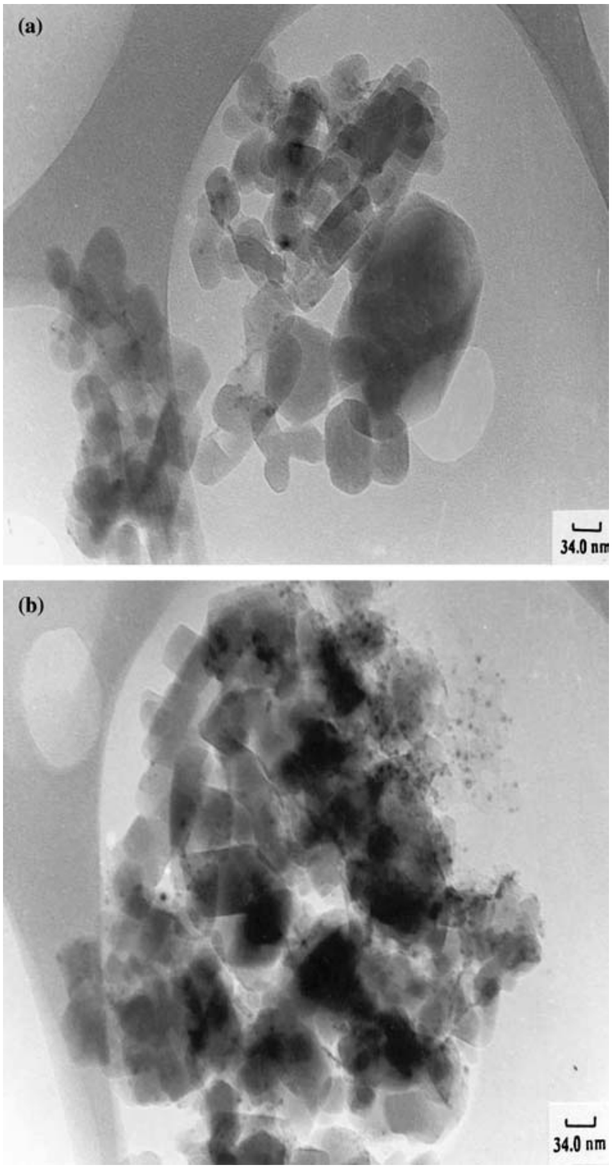

Figure 2. (a) TEM pictures of catalyst C_3. (b) TEM pictures of catalyst C_4.

possibility of overlap with Al 2p transition of support [25]. The ESCA spectra of Ni $2p_{3/2}$ peaks 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 catalysts C_4 indicate the presence of Ni^{2+} and the formation of $NiAl_2O_4$ from 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 Phi ESCA data book) [26, 27, 28]. An enhanced reduction of Ni^{2+} to Ni^0 by the addition of Pt was concluded by Malyala *et al.* [16] from their XPS study on Ni/Y-zeolite and Ni–Pt/Y-zeolite. Thus in the present case too the added Pt is supposed to favor the reduction of nickel cations in the region 0–0.3 wt% Ni above NiO is observed (for 0.5 wt%) in C series catalysts.

3.1.5. TGA–TPD of NH_3

The desorption of ammonia was carried out over C series catalysts by TGA method and the amount of ammonia desorbed from each of C series catalysts are presented in table 1. The model TGA-TPD curves for the typical catalyst C_3 is shown in figure 4. The temperature of desorption and amount of ammonia desorbed are the indexes of strength and number of acid sites [29]. There are two weight losses occurring at two different temperature ranges may be due to desorption of adsorbed ammonia on weak and strong acid sites. The first weight loss occurs from in the range of 150–180 °C. The second weight loss from occurs at 270–300 °C. From the table 1, it is found that low temperature desorption is always more than that at higher temperature. When Ni is added in increasing amount to the Pt loaded supports, the total acidity continuously falls. Jao *et al.* [15] in their TPD study of Pt/MOR systems observed the similar trend in acidity and accounted in terms of occupation of some of the acid sites of mordenite support by Ni species when increasingly loaded. When the Ni is brought into the Pt loaded zeolites by ion-exchange method, there is no significant change in acidity when compared with that of impregnated catalysts. This shows that Ni dispersion whether done by IWI or ion exchange, a definite amount of it occupy the acid sites and the best contributing to

Table 1
Physiochemical characteristics of C series catalysts

S. No.	Catalyst	Pt content (wt.%)	Ni content (wt.%)	BET surface area (m^2/g)	NH_3-TPD (mmol/g)		Total acidity (mmol/g)	Particle size (nm)
					LT-peak	HT-peak		
1	C_1	0.1	–	340	0.423	0.140	0.563	–
2	C_2	0.1	0.1	342	0.410	0.124	0.534	–
3	C_3	0.1	0.3	326	0.386	0.110	0.496	5.23
4	C_4	0.1	0.5	311	0.357	0.104	0.461	8.3
5	C_5[a]	0.1	0.1	328	0.364	0.117	0.481	–
6	C_6	–	0.5	335	0.346	0.126	0.472	–

LT: low temperature peak, HT: high temperature peak.

[a] Prepared by ion exchange method.

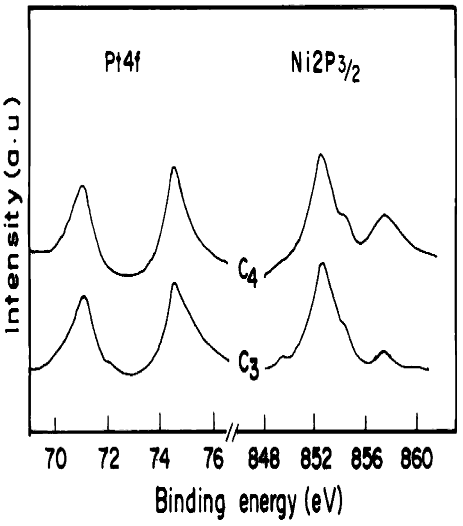

Figure 3. ESCA spectra of catalysts C_3 and C_4.

the growth of Pt–Ni particles. The low temperature and high temperature ranges observed in the NH_3 desorption process from all Pt, Ni and Pt–Ni loaded catalysts of the zeolite support lead to the conclusion that the acid strength of the acid sites on that support does not vary by addition of Ni.

3.1.6. *Pyridine adsorbed FT-IR spectroscopy*

The pyridine adsorbed FT-IR spectra of C (C_1, C_3 and C_4) series catalysts are shown in figure 5. A peak appeared around 1545 cm^{-1} on all the catalysts indicating the presence of pyridine adsorbed on Brønsted acid sites of zeolite. The pyridine adsorption on Lewis acid sites is indicated by another peak around 1455 cm^{-1}. The increasing addition of Ni in C 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. The decrease in the number of acid sites may be due to the occupation of acid sites by Ni species when increasingly loaded as observed in TPD-NH_3 studies. A board peak obtained around 1490 cm^{-1} indicating the physically adsorbed pyridine. The BET surface area (table 1) of the C series catalysts show a decreasing trend with increasing Ni addition, which may reflect the observation made in acidity measurement studies.

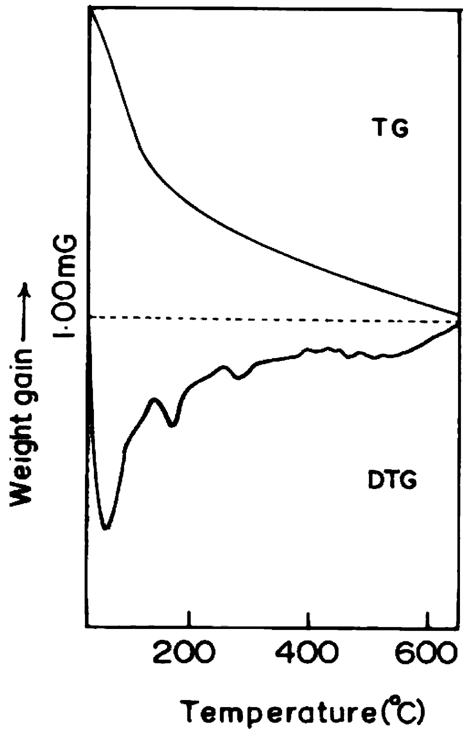

Figure 4. Typical TGA–TPD curves of catalyst C_3.

3.2. *Catalytic studies*

The toluene and 1,2,4-TMB disproportionation reactions were carried out separately over the reduced catalysts at LHSV = 1.33 h^{-1} in the temperature range 250–400 °C in steps of 50 °C. The product distribution of toluene and 1,2,4-TMB disproportionation are presented in Tables 2 and 3, respectively. It is invariably found that benzene, *p-,m-,o*-xylenes are the major products in toluene disproportionation and benzene, toluene, xylenes (*para, meta, ortho*), 1,3,5-TMB, 1,2,3-TMB and tetrametylbenzene (TeMB) are the major products in 1,2,4-TMB disproportionation.

3.2.1. *Effect of temperature*

The effect of temperature on toluene and 1,2,4-TMB conversion over all the catalytic systems is shown in figure 6(a) and (b), respectively. It is found that both the toluene and 1,2,4-TMB conversion increases with

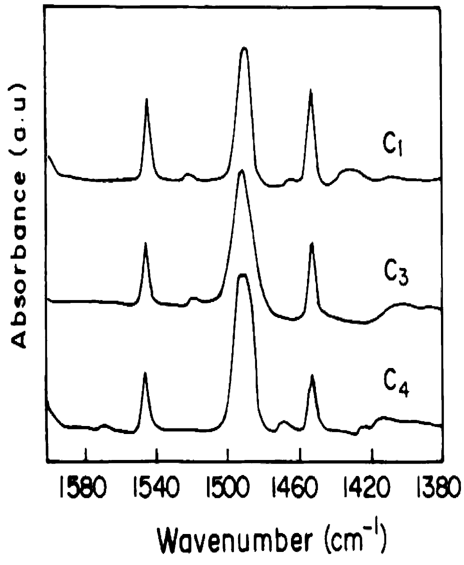

Figure 5. Pyridine adsorbed FT–IR spectra of C series.

Table 2
Product distributions of toluene disproportionation over C series catalysts at different temperatures

Product (wt.%)	250 °C						300 °C					
	C_1	C_2	C_3	C_4	C_5	C_6	C_1	C_2	C_3	C_4	C_5	C_6
Benzene	9.9	14.5	15.8	13.1	11.4	7.7	22.1	26.8	27.2	24.9	23.1	20.8
p-xylene	2.8	4.6	5.8	4.0	3.4	2.0	5.7	7.9	9.1	7.1	6.4	5.1
m-xylene	5.2	9.0	9.1	8.1	7.1	4.3	10.8	14.3	16.1	13.6	12.2	10.5
o-xylene	2.8	4.0	6.0	3.4	3.0	2.5	6.0	7.7	9.0	7.2	6.6	5.3
Others	0.2	0.1	0.1	0.1	0.2	0.3	0.5	0.3	0.2	0.2	0.3	0.6
Conversion	21.2	32.2	36.2	28.7	25.1	16.2	45.1	57.4	61.8	52.9	48.6	42.3
PX/Total xylene (wt%)	25.2	26.1	27.7	25.8	25.2	24.1	25.2	25.9	26.7	25.5	25.3	24.1
	350 °C						400 °C					
Benzene	24.0	28.8	30.1	26.7	25.6	2.22	27.1	34.1	34.6	32.2	30.4	25.1
p-xylene	6.0	8.3	9.6	7.8	6.6	5.3	6.1	9.0	10.2	8.1	6.8	5.2
m-xylene	12.2	16.3	18.0	15.1	14.0	11.5	15.2	18.1	19.2	17.2	16.3	13.0
o-xylene	6.6	8.1	9.3	7.2	6.2	5.7	6.6	9.3	10.3	8.5	7.8	6.4
Others	0.9	0.6	0.5	0.6	0.8	0.9	1.4	0.9	0.8	1.1	1.3	1.6
Conversion	49.7	62.1	67.5	58.4	53.2	45.6	57.4	71.4	75.1	67.1	62.6	52.3
PX/Total xylene (wt%)	24.1	25.4	26.0	25.0	24.6	23.5	21.9	24.7	25.7	23.9	22.0	20.3

Table 3
Product distributions of 1,2,4-trimetylbenzene disproportionation over C series catalysts at different temperatures

Product (wt%)	250 °C						300 °C					
	C_1	C_2	C_3	C_4	C_5	C_6	C_1	C_2	C_3	C_4	C_5	C_6
Benzene	0.02	0.04	0.03	0.01	0.02	0.02	0.07	0.09	0.10	0.08	0.10	0.05
Toluene	2.02	4.01	3.12	3.01	2.02	2.01	4.51	5.10	5.63	5.01	4.76	4.18
p-xylene	1.72	2.91	3.90	2.40	2.21	1.15	3.20	5.30	6.24	4.78	4.21	2.60
m-xylene	3.01	5.06	6.78	4.03	4.21	3.04	7.09	10.50	12.10	9.53	8.20	5.17
o-xylene	1.90	2.93	3.91	2.60	2.32	1.25	3.30	5.50	6.34	5.17	4.51	2.80
1,3,5-TMB	3.21	3.90	4.76	3.68	3.51	2.85	8.56	10.70	10.56	10.59	9.19	8.81
1,2,3-TMB	1.31	1.42	1.55	1.36	1.32	1.23	3.51	3.31	3.18	3.32	3.09	3.72
TeMB	1.01	1.03	1.05	1.01	1.03	0.95	2.26	2.01	2.05	1.62	2.78	2.37
Conversion	14.2	21.3	25.1	18.3	16.7	12.5	32.5	42.5	46.7	40.1	36.8	29.7
	350 °C						400 °C					
Benzene	0.08	0.10	0.17	0.12	0.15	0.09	1.03	1.16	1.05	1.09	1.21	0.95
Toluene	4.27	5.21	6.01	5.11	4.56	4.19	5.47	6.08	6.19	5.75	5.62	5.25
p-xylene	3.55	5.50	6.04	5.10	4.45	2.45	2.60	4.74	5.45	4.45	3.55	2.10
m-xylene	7.02	10.20	11.07	9.15	8.15	5.02	6.15	10.20	11.19	8.30	7.26	4.09
o-xylene	3.65	5.55	6.10	5.20	4.55	2.55	.75	4.82	5.55	4.55	3.65	2.30
1,3,5-TMB	12.14	12.05	13.05	11.56	11.70	12.58	15.82	15.23	15.01	15.52	15.68	16.10
1,2,3-TMB	4.44	4.01	4.15	4.05	4.20	4.71	5.17	4.73	4.65	4.82	5.02	5.26
TeMB	2.65	2.68	2.85	2.45	2.32	2.81	3.91	3.24	4.01	3.42	3.61	4.15
Conversion	37.8	46.3	47.3	42.7	40.1	34.4	42.9	50.2	53.1	47.9	45.6	40.2

increasing temperature over all the catalytic systems. The maximum conversion of toluene and 1,2,4-TMB over all the catalytic systems are observed at 400 °C. However, the disproportionation (xylenes) selectivity in both toluene and 1,2,4-TMB conversion over all the catalytic systems is found to decrease with increasing reaction temperature and is found to be a minimum at 400 °C. In the case of toluene, catalyst C_1 shows 21.2 wt% conversions with 52.4% disproportionation selectivity at 250 °C. On increasing the temperature to 300, 350 and 400 °C, the toluene conversion is increased to 45.1, 49.7 and 57.4 wt% with corresponding disproportionation selectivity 50.1, 49.9 and 48.6%, respectively. Similarly, for 1,2,4-TMB conversion is 14.2, 32.5, 37.8 and 42.9 wt% with corresponding disproportionation selectivity 46.7, 41.9, 37.6 and 26.8% were observed at 250, 300, 350 and 400 °C, respectively, over catalyst C_1. It is observed that the toluene conversion is always higher than that of 1,2,4-TMB over all the catalytic systems.

3.2.2. Effect of Ni addition on conversion of toluene

The effect of Ni addition on toluene and 1,2,4-TMB conversion can be studied by comparing the activity of Ni–Pt catalysts C_2, C_3, C_4 and C_5 with that of Ni free catalyst (catalyst C_1). The addition of 0.1 wt% Ni over catalyst C_1 increases the toluene conversion and disproportionation (xylenes) selectivity significantly at all the temperatures studied. Catalyst C_2 shows 32.2, 57.4, 62.1 and 71.4 wt% toluene conversion with corresponding disproportionation selectivity of 54.6, 53.1, 52.6 and 51.0% at 250, 300, 350, and 400 °C, respectively, which are significantly higher than that over catalyst C_1. Maximum toluene conversion of 71.4 wt% with 52.9% of disproportionation selectivity is observed over catalyst C_3 at 400°C. Further increase of Ni addition (catalyst C_4) leads to decrease in conversion as well as disproportionation selectivity at all temperatures studied. Catalyst C_4 shows 23.7, 52.9, 58.4 and 67.1 wt% toluene conversion with 54.0, 52.5, 51.5 and 50.4% of disproportionation selectivity at 250, 300, 350, and 400 °C, respectively, where are considerably less than that over catalyst C_3.

3.2.3. *Effect of Ni addition on conversion of 1,2,4-TMB*

In the case of 1,2,4-TMB, maximum conversion of 53.1 wt% is observed over catalyst C_3 at 400 °C and disproportionation selectivity of 54.3, 52.9, 47.3 and 43.7% at 250, 300, 350, and 400 °C, respectively, which are considerably higher than that over catalyst C_1. The disproportionation selectivity is found to increase with increasing Ni addition up to 0.3 wt%, similar to the observation made for toluene disproportionation over catalyst C_3. Further increase of Ni addition (catalyst C_4) leads to a decrease in 1,2,4-TMB conversion as well as disproportionation selectivity.

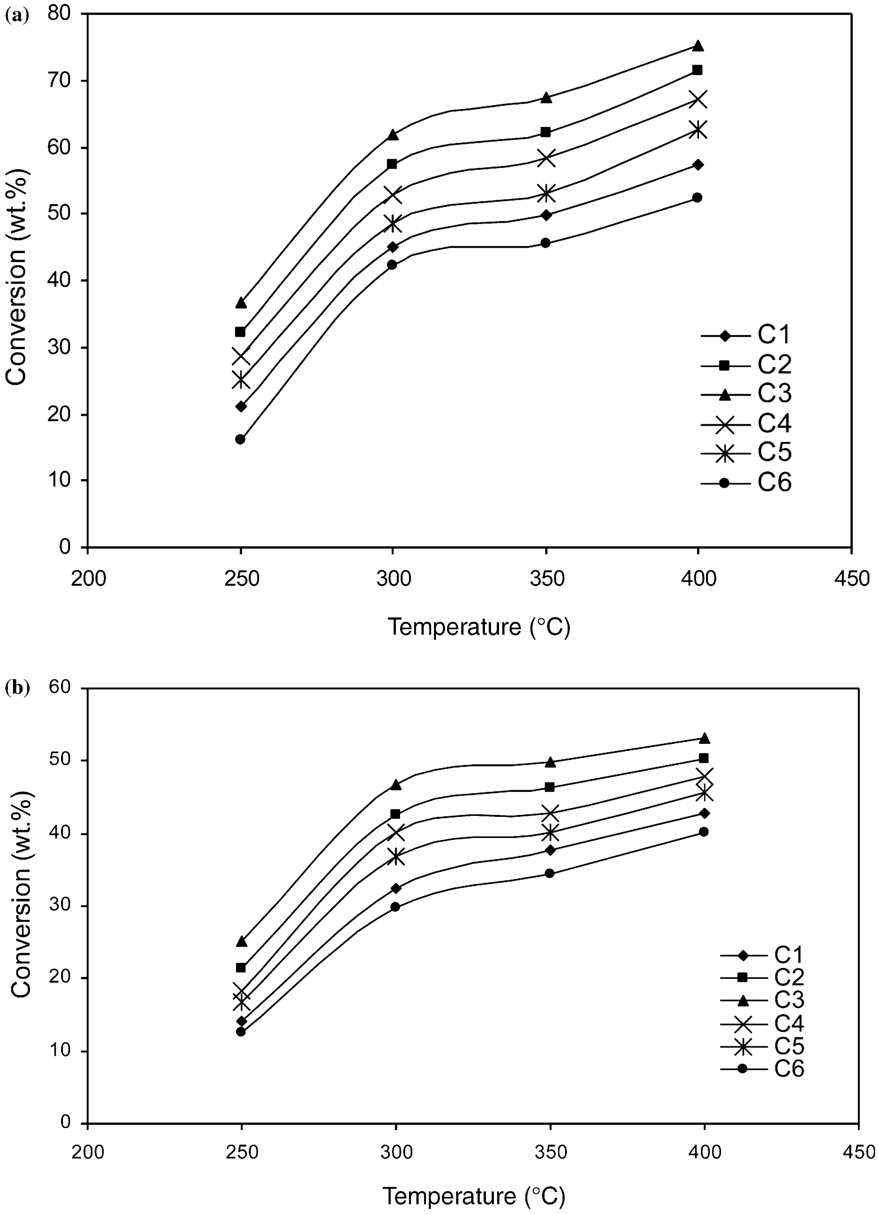

Figure 6. (a) Effect of temperature on toluene over C series catalysts; (b) Effect of temperature on 1,2,4-trimethylbenzene over C series catalysts.

3.2.4. *Effect of Ni-Pt bimetallic particles*

The maximum activity and selectivity observed on catalyst C_3 may be due to the better metal-acid synergism between bimetallic (Ni–Pt) particles as evidenced by TEM and acid sites of the support. The TEM study shows that the average metal particle size of catalyst C_3 is 5.23 nm and the ESCA study confirms the complete reduction of Ni and Pt species, which are active in hydrogenation–dehydrogenation steps. The initial increase in conversion and disproportionation selectivity in both toluene and 1,2,4-TMB disproportionation with increasing Ni addition up to 0.3 wt% can be accounted in terms of the added Ni possibly increasing the number of active metallic sites/acid sites ratio towards the optimum value for the disproportionation/isomerization reactions [30]. The decrease in selectivity of dialkylated isomers formation on larger sized (8.3 nm) bimetallic particles by TEM as well as unreduced Ni as evidenced by ESCA studies, respectively. This disturbs the better metal balance leading to poor activity. The catalysts with higher average particle size may hinder the movement of bulk intermediate in the pores of zeolite-Y.

Also in our previous study [21], 0.3 wt% Ni–0.1 wt% Pt/H-β and 0.1 wt% Ni–0.1 wt% Pt/H-MOR showed an enhanced activity in *n*-heptane conversion, DMB selectivity and sustainability of the catalysts. Further addition of Ni leads to decrease in conversion and DMB selectivity and is accounted for in terms of better synergism between catalytically active bimetallic (Ni–Pt) nanoparticles formed in acid sites of the supports.

3.2.5. *Effect of temperature on product selectivity of toluene*

The effect of temperature on the selectivity of individual isomers of toluene and 1,2,4-TMB over the best performing catalyst (C_3) is shown in figure 7(a) and (b), respectively. Generally, the selectivity of the dialkylated isomers *p*-, *m*-, *o*-xylenes are found to decrease with increasing temperature as well as conversion over all the catalytic systems. The fall in selectivity of *p*-xylene is more than that of *o*-xylene. Also, the selectivity of *p*-xylene is found to be always higher than that of *o*-xylene. At 250 °C abrupt increase in *p*-xylene is observed, this may be due to favorable temperature for diffusion of para isomer and better synergism between metal and acid sites [31–33]. The selectivity of *m*-xylene increases with increasing temperature. At 250–400 °C the xylene isomers are in thermodynamic equilibrium ratio. The decrease in the total xylene selectivity and increasing in *m*-xylene selectivity with increasing temperature suggest that the transformations are *p*-, *o*-xylene to *m*-xylene or benzene. Proposed Mechanism for toluene disproportionation on bifunctional Ni–Pt/Y-zeolite showed in Scheme 1(a) Methyl transfer mechanism (b) and bimolecular mechanism.

3.2.6. *Effect of temperature on product selectivity of 1,2,4-TMB*

The effect of temperature on the selectivity of 1,2,4-TMB, increases the selectivity of toluene and benzene with increasing temperature as well as conversion over all the catalytic systems. The fall in selectivity of dialkylated isomer *p*-xylene is more than that of *o*-xylene. It is observed that dialkylated to tetraalkylated products are significantly greater than one [14]. The selectivity of isomerized feed isomers 1,3,5-TMB is higher that of 1,2,3-TMB on all the systems. The selectivity of TeMB is found to increases with increasing temperature [34]. According to the above results, a simplified reaction scheme 2 for the transformation for the 1,2,4-TMB.

3.2.7. *Effect of Ni addition on p-xylene/Total xylenes ratio*

The effects of Ni addition on *p*-xylene/Total xylenes (PX/Total xylenes) ratio on toluene disproportionation at various temperatures are presented in table 2. It is observed that PX/Total xylenes ratios are found to increase with Ni addition and the increase is continued up to 0.3 wt% at all temperatures studied, i.e. *p*-xylene selectivity is enhanced upto 0.3 wt% Ni addition. The PX/Total xylene ratios over catalyst C_3 are 27.7, 26.7, 26.0 and 25.7 at 250, 300, 350, and 400 °C, respectively, which is more than thermodynamic equilibrium values [35]. Further Ni addition (catalyst C_4) leads to decrease in the PX/Total xylenes ratio, i.e. a decrease in para selectivity.

3.2.8. *Effect of Ni addition on disproportionation selectivity of 1,2,4-TMB*

Similarly, in the case of 1,2,4-TMB, the 1,3,5-/1,2,3-TMB ratios are found to increase with increasing Ni addition up to 0.3 wt%. The disproportionation selectivity (xylenes) over the best performing catalyst (C_3) is 54.1, 52.9, 47.3 and 43.7 at 250, 300, 350, and 400 °C, respectively, which are much different from the values (32.6 at 350 °C) reported by Se-Ho park *et al.* [13].

The suitability of any catalyst for disproportionation reactions are measured by its disproportionation/isomerization (D/I) ratio. A good disproportionation catalyst should have a very high D/I ratio. The effect of Ni addition on dialkylated isomers selectivity in toluene and 1,2,4-TMB conversion at various temperatures is shown in figures 8(a) and (b), respectively. It is observed that increasing Ni addition up to 0.3 wt% increases the xylene isomers selectivity, which decreases thereafter. The enhanced disproportionation selectivity of catalyst C_3 may be accounted in terms of its better metal-acid balance, bimetallic (Ni–Pt) nanoparticle formation and complete reduction of Ni and Pt species.

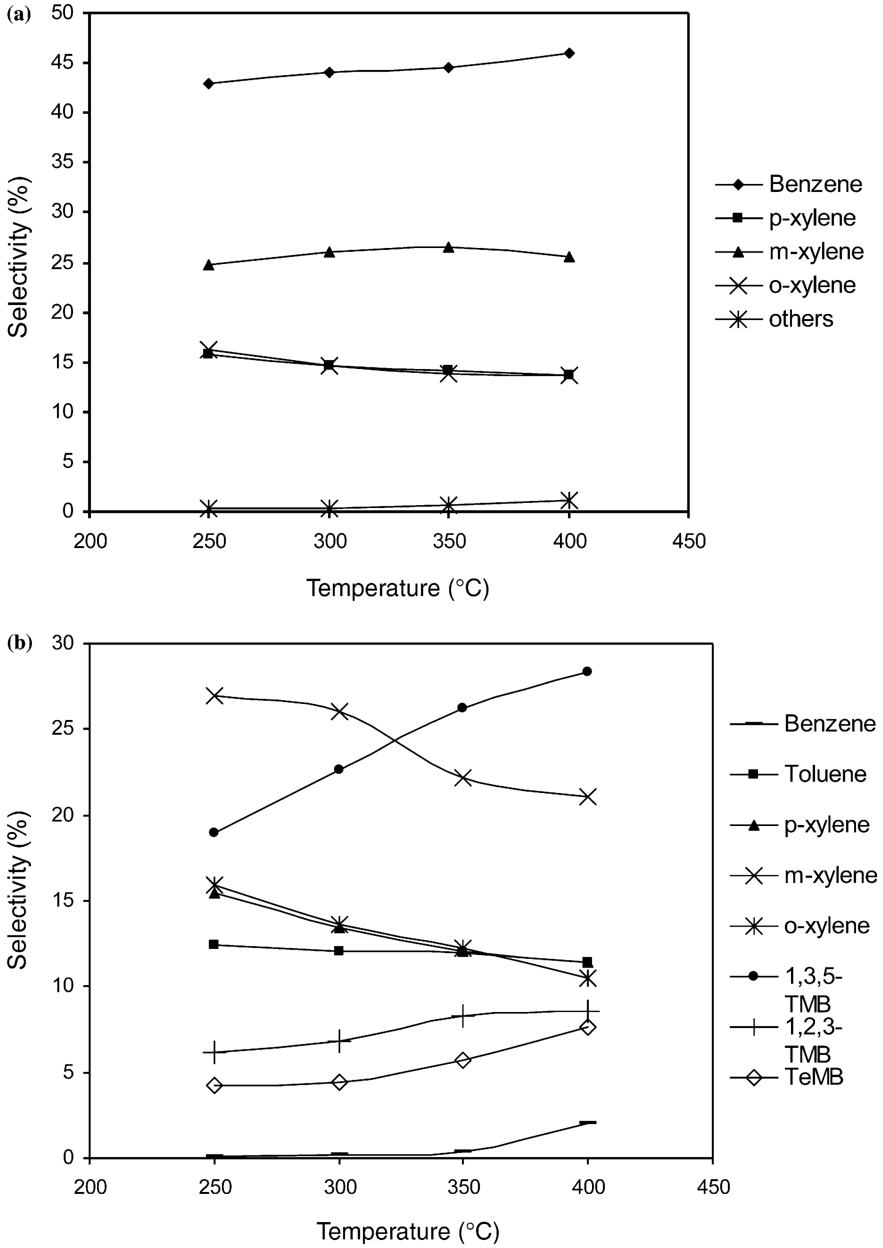

Figure 7. (a) Effect of temperature on the selectivity of toluene isomers over C_3 catalyst; (b) Effect of temperature on the selectivity of 1,2,4-trimethylbenzene isomers over C_3 catalyst.

3.2.9. Effect of time on stream

A time-on-stream study for a period of 6 h at 350 °C was carried out all over the catalysts in order to study the sustainability of the catalysts. In both reactions all the catalysts shows decreases in conversion with time, which showed in figure 9(a) and (b). Here also, catalyst C_3 dominating on other catalysts. Catalyst C_1 and C_6 shows a rapid decrease in conversion for both toluene and 1,2,4-TMB disproportionation with time. This rapid decrease in activity can be accounted in terms of coke formation, which may block the active sites leading to lower activity.

Another reaction like time-on-stream is carried out for the formation of coke on catalyst surface. 8.89 g of reactant was fed onto 1 g of the C_3 catalyst and this was left on-stream for 5 h. It showed that 7.50 g (84.36%) of reactant was converted to products at the end of 5 h on-stream. Out of the remaining 1.39 g (15.64%) of reactant, an amount of 0.19 g (2.14%) of reactant was transformed into coke. The weight loss of 1.20 g (13.5%) of reactant will be probably due to C_1–C_4 molecules gaseous products formation.

4. Conclusion

The line broadening XRD analysis shows that the crystallinity of the zeolite decreases with increasing Ni loading. The TEM images of Ni–Pt/H–Y zeolite

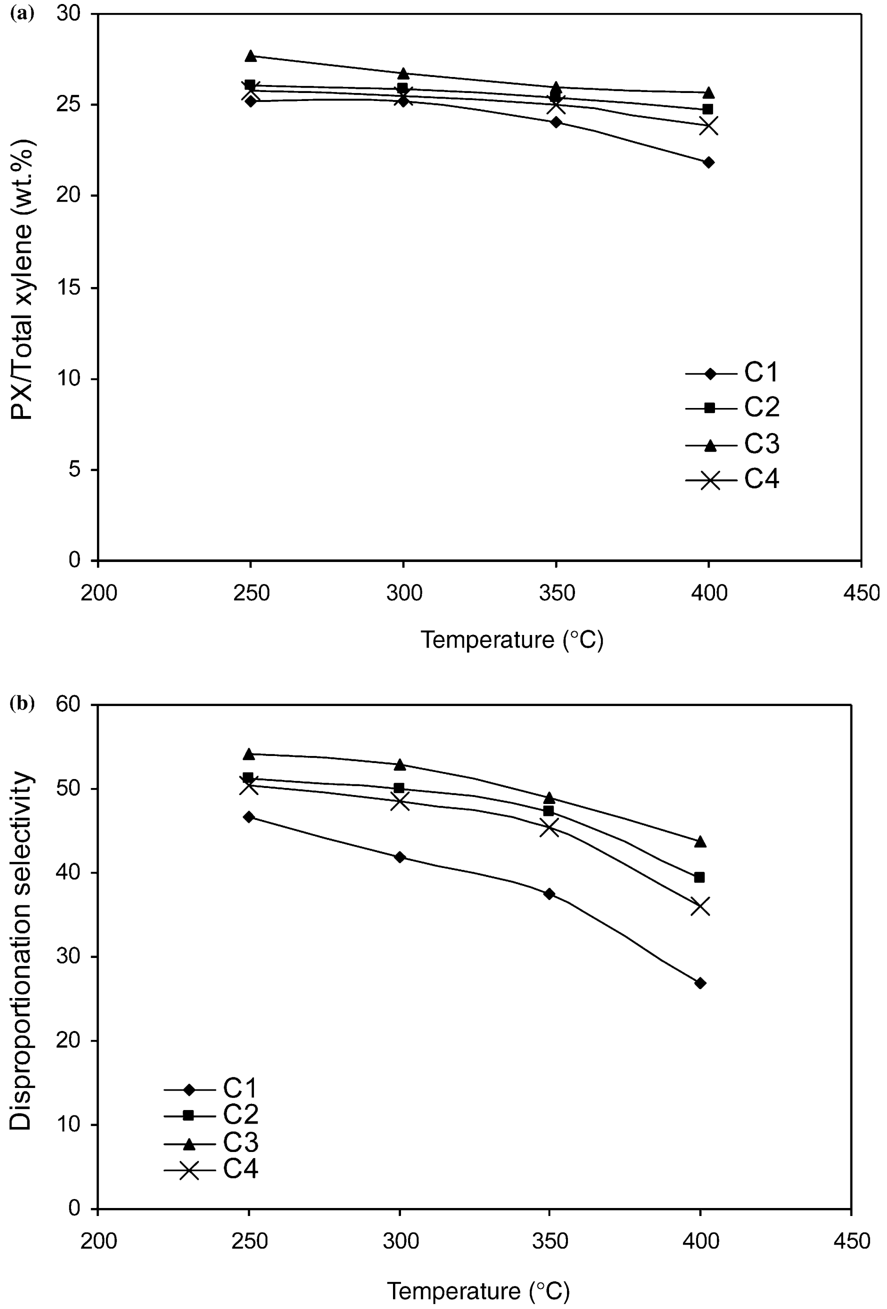

Figure 8. (a) Effect of Ni addition on PX/Total xylene ratio of catalysts in toluene at various temperatures; (b) Effect of Ni addition on disproportionation selectivity of catalysts in 1,2,4-trimethylbenzene at various temperatures.

catalysts show the formation of bimetallic (Ni–Pt) particles of nanometer scale. Also, it is found that the average particle size of bimetallic particles increases with increasing Ni loading. The XPS study on Ni–Pt/H–Y reveals that complete reduction of Ni occurs up to 0.3 wt% and further Ni addition leads to the occurrence of unreduced Ni as $NiAl_2O_4$. The acidity measurements of Ni–Pt/H–Y by NH_3-TPD and pyridine-adsorbed FTIR spectroscopy studies show that the increasing addition of Ni decreases the total acidity of the catalysts but does not affect the acidic strength of Ni–Pt/H–Y catalysts. Because of the best synergistic effect, the 0.3 wt% Ni–0.1 wt% Pt/H–Y catalyst shows an enhanced activity in both toluene and 1,2,4-TMB disproportionation. Further Ni addition leads to a decrease in activity. Also, the 0.3 wt% Ni addition enhanced the disproportionation selectivity, diphenylmethane intermediate formation mechanism and sustainability of the catalysts in both toluene and 1,2,4-TMB disproportionation. The enhanced activity of 0.3 wt% Ni–0.1 wt% Pt/H–Y may be due to better metal-acid balance, formation of catalytically active bimetallic

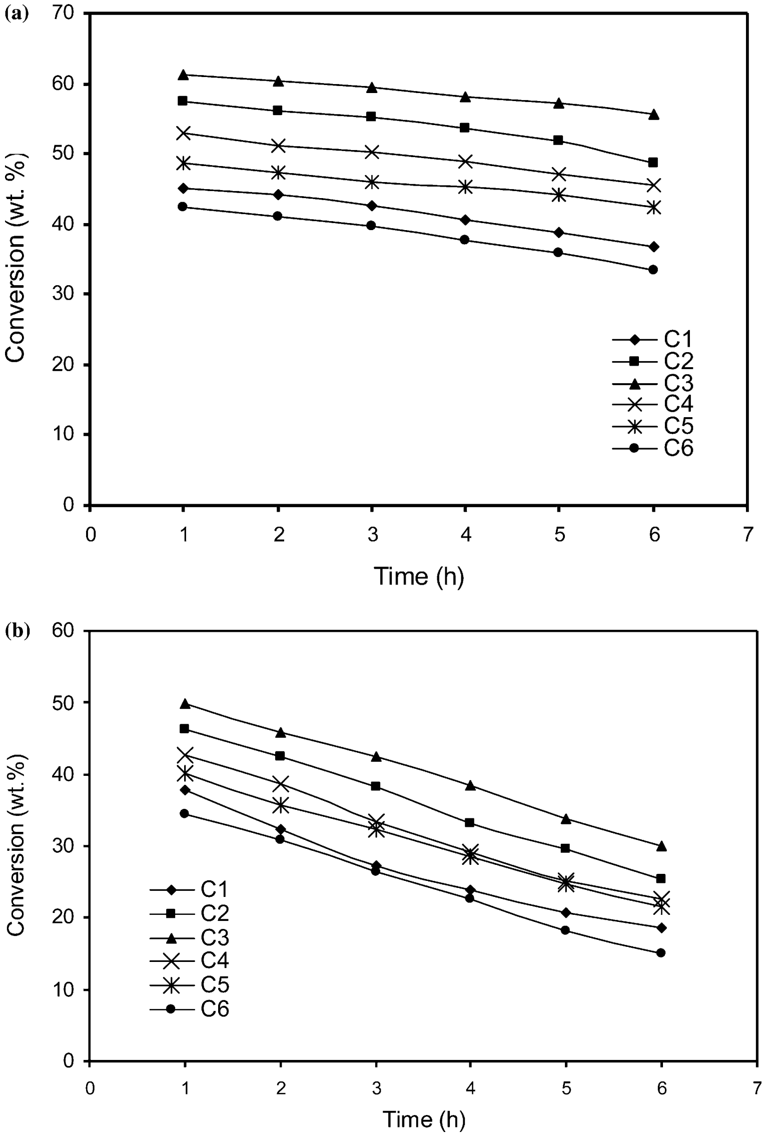

Figure 9. (a) Effect of time on stream on toluene disproportionation; (b) Effect of time on stream on 1,2,4-trimethylbenzene disproportionation.

(Ni–Pt) particles of nanoscale size and complete reduction of Ni and Pt species.

References

[1] I.E. Maxwell and W.H.J. Strok, Stud. Surf. Sci. Catal. 58 (1991) 571.
[2] H.W. Kouwenhoren and W.C. Zijll Langhout, Chem. Eng. Prog. 67 (1971) 65.
[3] R.J. Toylor and R.H. Petty, Appl. Catal. 119 (1994) 121.
[4] A. Gil, A. Diaz, L.M. Gandia and M. Montes, Appl. Catal. 109 (1994) 167.
[5] D.L. Hong, H. Berndt, H. Missner, E. Schereier, J. Volter and Santen van, Ind. Eng. Chem. Res. 34 (1995) 55.
[6] J.M. Ward, Fuel Process. Technol. 32 (1993) 55.
[7] P. Gallezot, Catal. Rev. Sci. Eng. 21 (1979) 121.
[8] L.C. Gutberlet and R.J. Bertolacini, U.S. Pat., 3, 548, 020 (1970).
[9] E. Kikuchi, R. Hirogari, T. Kimura and Y. Morita, Bull. Japan. Petrol. Inst. 15 (1973) 129.
[10] W.U. Jung-Cung and L.E.U. Li-Jen, Appl. Catal. 7 (1983) 283.
[11] R.P. Dimitrova, C.H.R. Dimitrov, Z. Popova and K.H. Steinberg, Appl. Catal. 3 (1982) 377.
[12] E. Kikuchi, E. Matsuda, J. Ueda and Y. Morita, Appl. Catal. 16 (1985) 401.
[13] S.-Ho Part and Hyun-Ku Rhee, Catal. Today 63 (2000) 267.
[14] H.P. Roger, K.P. Moller and C.T. O'Connor, J. Catal. 176 (1998) 68.
[15] R.M. Jao, T.B. Lin and J.R. Chang, J. Catal. 161 (1996) 222.
[16] R.V. Malyala, C.V. Rode, M. Arai, S.G. Hegde and R.V. Chaudhari, Appl. Catal. 193 (2000) 71.
[17] M.A. Jordao, V. Simoes, A. Montres and D. Cardoso, Stud. Surf. Sci. Catal. 130 (2000) 2387.
[18] A.M. Dominguez, A. Vazquez, A.J. Renouprez and M.J. Yacaman, Surf. Sci. 75 (1982) 101.
[19] I. Eswaramoorthi and N. Lingappan, Appl. Catal. 245(2) (2003) 119.
[20] M.M.J. Treacy and J.B. Higgins, *Collection of Simulated XRD Powder Patterns of Zeolites* 4 ed.(Elsevier, Amsterdam, 2001).
[21] I. Eswaramoorthi, A. Geetha Bhavani and N. Lingappan, Appl. Catal. 253 (2003) 469.
[22] I. Eswaramoorthi and N. Lingappan, Korean J. Chem. Eng. 20(3) (2003) 207.

[23] P. Canizares, A. de Lucas, F. Dorado, A. Duran and I. Asencio, Appl. Catal. 169 (1998) 137.

[24] D.J. Ostard, L. Kustov, K.R. Poeppelmeier and W.M.H. Sachtler, J. Catal. 133 (1992) 342.

[25] M.A. Arribas, F. Marquez and A. Martinez, J. Catal. 190 (2000) 309.

[26] Ch. Minchev, V. Knazirev, L. Kosova, V. Pechev, W. Grunsser and F. Schimidt, in: L.V.C Rees ed. Proceedings of the Fifth International Conference on Zeolite, Heydon, London, 1980, p. 335.

[27] S. Narayanan and Zeolites, 4(3) (1984) 231.

[28] S. Xiao and Z. Meng, J. Chem. Soc. Faraday Trans. 90(17) (1994) 2591.

[29] L.-J. Leu, L.-Y. Hov, B.-C. Kang, C. Li, S.-T. Wu and T.-C. Wu, Appl. Catal. 69 (1991) 49.

[30] E. Blosnsma, J.A. Martens and P.A. Jacobs, J. Catal. 155 (1995) 141.

[31] N.Y. Chen, W.W. Kaeding and F.G. Dwyer, J. Am. Chem. Soc. 101 (1979) 6783.

[32] W.W. Kaeding, C. Chu, L.B. Young and S.A. Butter, J. Catal. 69 (1981) 392.

[33] L.B. Young, S.A. Butter and W.W. Kaeding, J. Catal. 69 (1981) 392.

[34] N.S. Gnep, J. Tejada and M. Guisnet, Bull. Soc. Chim. Fr. 1-2 (1982) 15.

[35] H.W. Earhart, *Polymethylbenzenes, Kirk-Othmer Encyclopedia of Chemical Technogy* (Wiley, New York, 1982)vol. 18.