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Article

Effect of metal content on the activity and product selectivity of *n*-decane hydroisomerization over Ni-Pd/HY zeolite

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ABSTRACT

Metal-loaded zeolite catalysts were synthesized and examined in the hydroisomerization of *n*-decane. Specifically, zeolite Y was impregnated with 0.1 wt% Pd and varying amounts of Ni (0.1–0.5 wt%). The crystallinity of the metal-loaded catalysts was characterized by X-ray diffraction, and the average metal particle size was determined by transmission electron microscopy. The states of Pd and Ni were identified by X-ray photoelectron spectroscopy. Ammonia temperature-programmed desorption analysis revealed the occurrence of ion-exchange of some of the catalyst acid sites with Ni²⁺. The reducibility of the HY zeolite-supported Pd, Ni, and Pd-Ni catalysts was studied by temperature-programmed reduction. The hydroisomerization of *n*-decane over the prepared catalyst was conducted at 200–450 °C under 1 atm. Ni addition of up to 0.3 wt% over 0.1 wt% Pd/HY enhanced the *n*-decane conversion and isomerization product selectivity. The improved selectivity of the mono- and dibranched isomers suggested the occurrence of a protonated cyclopropane intermediate mechanism. However, further Ni addition above 0.3 wt% considerably reduced the activity and isomerization selectivity. The bimetallic catalysts were more selective toward the formation of dibranched isomers, i.e., those containing a higher octane number.

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1. Introduction

Bifunctional catalysts with metallic and acidic functionalities are commonly used in numerous industrial processes in petroleum refining and the petrochemical industry [1,2]. Transition metals can catalyze reactions such as isomerization, (de)hydrogenation, hydrogenolysis, aromatization, and cyclization of hydrocarbons [3]. However, their ability to chemisorb hydrogen, hydrocarbons, and other molecules varies with the chemical nature of the element [4]. Pt and Pd are the most important transition metals used in catalysis and can catalyze diverse hydrocarbon reactions [5–7]. γ -Al₂O₃ is a typical acid

component present in commercially used reforming catalysts. However, zeolites are gaining increasing attention for application in processes such as hydroisomerization, hydrocracking, and dewaxing [8–11]. In the presence of bifunctional catalysts, dehydrogenation (hydrogenation) of hydrocarbons occurs on the metal sites, whereas isomerization and C–C bond cleavage occur on the Brönsted acid sites [12–14]. Hence, the balance between the metallic and acidic sites is important because it determines the activity of the reaction, stability of the catalyst, and selectivity of the product. Considerable efforts have been invested in understanding the reaction mechanism, which leads to the formation of isomers as well as cracked products from

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normal and branched paraffins over bifunctional zeolites [15–17]. According to the classical isomerization mechanism [13,18], paraffins are dehydrogenated on the catalyst metal sites, and the formed olefins are protonated on the acid sites to the corresponding alkylcarbenium ions. These carbenium ions undergo skeletal rearrangement and β -scission followed by deprotonation and hydrogenation to the corresponding paraffins over the metal sites. The selectivity of paraffin isomerization (defined as the ratio of the isomerized to the cracking products) depends primarily on the balance between the metal and acid catalyst functions that control the rate of the isomerization and β -scission reactions.

Arifulin et al. [19] studied the effect of organic compound impurities on the hydroisomerization of decane over a Pd-based catalyst. The results showed that the presence of 1-octene, decalin, ethylbenzene, or naphthalene (2 mol/L) had negligible effects on the activity of an aluminopalladium sulfide catalyst in the hydroisomerization of decane at 40 atm and 400 °C. However, the isomerization of decane decreased by 20%–25% in the presence of 10 mol% ethylbenzene and naphthalene mixtures. The presence of acenaphthene, benzothiophene, or aniline (2 mol%) prevented the reaction from proceeding. Martens et al. [20–22] examined the isomerization of decane over 0.5%–1% Pt supported on ferrierite, BETA, and Y zeolites. The product distribution obtained over the ferrierite catalysts differed from that over the two remaining catalysts. This result suggested that the BETA and Y zeolite catalysts featured the same void volume structure. Small variations in the physicochemical properties of a given zeolite structure do not significantly influence the product distribution. The product distribution pattern is the only accurate information on the pore size and structure. Alvarez et al. [23] demonstrated a quantitative relationship between activity, stability, and product selectivity in the hydroisomerization and hydrocracking of *n*-decane over bifunctional Pt/HY catalysts and the ratio of the number of metallic sites to the number of acid sites. In the presence of abundant acid sites, direct *n*-decane isomerization and cracking into the corresponding products occurred. When the number of acid sites was below 6, *n*-decane transformed successively into monobranched isomers, dibranched isomers, and cracking products. In the latter case, the catalysts can be considered as ideal bifunctional catalysts as there are no reaction limitations by the hydrogenation and dehydrogenation steps or the migration of olefinic intermediates between hydrogenating sites. Therefore, the activity per acid site is maximal, and the apparent reaction scheme matches the transformation scheme of olefinic intermediates. Zakumbaeva et al. [24] investigated the effect of decationized forms of zeolites (HZSM, HY, and clinoptilolite) and reaction temperature on the hydrocracking and hydroisomerization activity of zeolite-containing catalysts modified by metals in the conversion of *n*-decane. GK-3 catalyst based on high-silica HZSM-zeolite displayed the highest hydrocracking, hydroisomerization, and hydrodesulfurization activity and selectivity. Elangovan et al. [25] examined the hydroconversion of *n*-decane over bifunctional catalysts comprising bimetallic Pt-Pd clusters supported on an AIMCM-41 (Si/Al = 23) mesoporous molecular sieve. The

catalytic activity of the bimetallic Pt-Pd catalysts was higher than that of the monometallic Pt and Pd catalysts. Additionally, the good balance between the two catalytic functions, namely acid sites and metal sites, afforded a higher isomer yield at a substantially lower reaction temperature. Moreover, cracking on the metal sites (hydrogenolysis) was largely suppressed over certain bimetallic catalysts. Rezgui et al. [26] reported the hydroconversion of *n*-decane over Ni-W/SiO₂-Al₂O₃ with different Ni and W concentrations (12%–17% Ni and 8%–30% W). *n*-Decane isomerization and cracking to the corresponding products were dependent on both the metal content (up to 15% of Ni) and acid sites. The extent of isomerization increased subsequently owing to imbalance in the metal-to-acid sites content. The combination of 15% Ni and 10% W provided optimum balance between the acid and metal functions, realizing 42.3% of *n*-decane conversion and 55% of isomerization product selectivity at 100 min of reaction.

To date, few reports are available in the literature that examine the addition of Ni as the second metal to Pd; moreover, high Ni loadings (≥ 1.0 wt%) have been typically studied. In the present study, nickel was introduced as the second metal at low concentrations (< 1.0 wt%) to modify the catalytic properties of Pd-supported zeolite Y toward *n*-decane hydroisomerization. Additionally, variations in the product distribution were examined in terms of metal loading, and reaction temperature and activity.

2. Experimental

2.1. Catalyst preparation

The sodium form of zeolite Y (SiO₂/Al₂O₃ = 6) was supplied by United Catalyst India Ltd., India. HY was obtained by repeated ion-exchange of zeolite Y with aqueous 1 mol/L NH₄Cl solution followed by calcination at 550 °C for 5 h. HY was then loaded with 0.1 wt% Pd by incipient wetness impregnation (IWI), and the resulting material is referred to as catalyst B₁. Then, B₁ was impregnated by IWI with 0.1, 0.2, 0.3, 0.4, and 0.5 wt% Ni, and the resulting samples are designated as B₂, B₃, B₄, B₅, and B₆, respectively. For comparison purposes, 0.3 wt% Ni was prepared by the IWI method, and the resulting material is designated as catalyst B₇. Aqueous solutions of palladium chloride (Sisco Research Laboratory, India) and nickel nitrate (Central Drug House, India) were used as sources of Pd and Ni, respectively. The metal-loaded catalysts were dried at 120 °C for 24 h. Then, the catalysts (1 g) were packed in a quartz reactor and activated at 550 °C for 3 h under N₂ atmosphere. The temperature was then lowered to 475 °C under hydrogen flow (30 mL min⁻¹ g⁻¹) for 6 h to reduce the metal ions.

2.2. Characterization

2.2.1. X-ray diffraction (XRD) measurements

The purity of the HY and metal-loaded zeolites was analyzed by XRD on an X'Pert X-ray diffractometer, operating with Ni-filtered Cu K α radiation ($\lambda = 1.54$ Å) in the scan range of $2\theta = 5^\circ$ – 50° .

2.2.2. Surface area measurements

The specific surface area of the catalysts was determined by nitrogen sorption using the Brunauer-Emmett-Teller method; the nitrogen sorption data were acquired on a Quantachrome Autosorb automated gas sorption instrument. Prior to the measurements, all samples were degassed at 400 °C for 6–8 h under a flow of N₂ at 60 mL/min.

2.2.3. Temperature-programmed desorption of ammonia (NH₃-TPD) analysis

The concentration of acid sites of the catalysts was measured by NH₃-TPD on a Micromeritics TPD/TPR 2900 analyzer. The catalysts (150 mg) were housed in a quartz tubular reactor and pretreated in flowing helium ($\geq 99.999\%$ purity) while heating to 550 °C at 10 °C/min. After maintaining the temperature for 30 min, the catalysts were cooled to 210 °C and saturated for 15 min in an ammonia stream ($\geq 99.999\%$ purity). The catalysts were then allowed to equilibrate in a flow at 210 °C for 1 h. Then, ammonia was desorbed by heating the catalysts at 800 °C at a linear heating rate of 15 °C/min. The temperature and detector signals were recorded simultaneously. The area under the obtained curve was integrated to determine the relative total acidity of the catalysts. Weak and strong acidities, as measured by the concentration of weak and strong acid sites, respectively, were determined by integration of the area under the peaks at the lowest and the highest temperatures, respectively [27,28].

2.2.4. Temperature-programmed reduction (TPR) measurements

TPR measurements were performed using the same apparatus as that used for the TPDA analysis. After metal loading, the sample (150 mg) was degassed by heating to 550 °C at 30 °C/min in an argon flow, after which the temperature was maintained for 30 min. Then, the sample was cooled to room temperature and stabilized under an argon/hydrogen flow ($\geq 99.999\%$ purity, 85:15 v/v). The temperature and detector signals were then continuously recorded while heating to 550 °C at 20 °C/min. The liquids formed during the reduction process were collected by a cooling trap positioned between the sample and detector.

2.2.5. X-ray photoelectron spectroscopy (XPS) analysis

The oxidation state of palladium and nickel in catalysts B₄ and B₆ was reduced at 475 °C for 6–7 h and analyzed by XPS. The XPS spectra were acquired on a surface analysis system (KRATOS ESCA model AXIS 165) using Mg K α radiation (1253.6 eV) and a pass energy of 50 eV. During spectral acquisition, the pressure of the analysis chamber was maintained at $<1 \times 10^{-7}$ torr.

2.2.6. Transmission electron microscopy (TEM) analysis

TEM analysis of the reduced catalysts was conducted on a JEM-2000 FX-II-JEOL electron microscope, operating at 300 kV. Specimens were enlarged using a thin photographic paper. The size of all the metal particles visible in each photograph was measured manually and averaged.

2.3. Catalytic studies

The catalytic reactions were performed in a fixed-bed continuous down-flow quartz reactor under 1 atm. About 1 g of the metal-loaded catalysts was packed in the reactor, which was then introduced into 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⁻¹ g⁻¹) for 3–6 h. After the reduction process, the temperature was lowered to the reaction temperature. The reactant *n*-decane was fed into the reactor by a syringe pump at a liquid hour space velocity (LHSV) of 2 h⁻¹, and pure hydrogen gas at a flow rate of 20 mL min⁻¹ g⁻¹ was flowed. The reaction gas mixture was heated in the temperature range of 200–450 °C. The obtained products flowed through a condenser, which was attached to the end of the reactor, under ice-cold conditions and were collected in a trap kept in ice at time intervals of 1 h. The products were then analyzed on an AIMIL NUCON 5765 gas chromatograph equipped with a PIONA column and a flame ionization detector and identified by gas chromatography-mass spectrometry (PerkinElmer QP5000).

3. Results and discussion

3.1. Characterization

3.1.1. XRD

The XRD pattern (not shown) of zeolite Y featured intense diffraction peaks within a 2θ range of 2°–50°, which are in good agreement with those displayed by the standard reference [29]. The XRD patterns of the metal-loaded zeolite catalysts are shown in Fig. 1. As observed, the intensity of the XRD peaks decreased with increasing Ni added amounts. Specifically, the intensity of the XRD peaks of B₂–B₇ at $2\theta = 6.13^\circ, 15.49^\circ, 23.51^\circ, 24.39^\circ, 26.83^\circ, 31.13^\circ,$ and 43.05° decreased with increasing Ni added amounts likely because of pore blockage by the Ni species. Intense peaks of Pd (111, 200), Ni (cubic), and NiO (hexagonal) are known to appear at 2θ values of 40°, 46.5°, 44.5°, and 43.3°, respectively, as reported by Fagherazzi et al. [30] and

Fig. 1. XRD patterns of B series catalysts.

Fig. 2. NH_3 -TPD curves for B₁, B₄, B₆ and B₇ catalysts.

Cullity et al. [31]. However, these peaks were not detected in the present study, suggesting that the size of the metal particles is below the detection limit of the XRD technique.

3.1.2. NH_3 -TPD

The NH_3 -TPD profiles, characterizing adsorbed NH_3 on the different catalysts, are shown in Fig. 2. The position of the peaks varied considerably depending on the metal loading. However, in all cases, two peaks were observed at ~ 343 and 518 °C. These two peaks could be attributed to the desorption of ammonia from weak and strong acid sites, respectively. The amount of desorbed ammonia and the desorption temperature were considered as a measure of the total acidity and acid strength of the catalysts, respectively [32]. As observed from Table 1, the amount of ammonia adsorbed at the lower temperature (indicative of weak acidity) was always greater than that adsorbed at the higher temperature (indicative of strong acidity). Furthermore, a higher Ni loading decreased the total acidity of the bimetallic catalysts. The decrease in acidity of the bimetallic catalysts with higher nickel loadings could be attributed to the occupation of some acid sites by the added nickel species [33–36]. In addition, this result could also be related to Ni combining with the Pd particles and the likely growth of the Ni-Pd particles. The same results have been reported in our previous work [36]. Furthermore, as observed in Table 1, the surface area of the catalysts decreased slightly with increasing

Fig. 3. TPR curves for B₁, B₄, B₆ and B₇ catalysts.

Ni loading. This result suggested partial blocking of the zeolite channels by the nickel species [37]. Moreover, a study [38] reported a decrease in acid site density and surface area when Ni was introduced in mordenite zeolite, which was also attributed to partial pore blockage by the Ni particles. As mentioned earlier, the peak temperature, corresponding to the ammonium desorption profile, was marginally influenced by an increase in Ni loading, indicating that the Ni content only slightly affected the strength of the acid sites (Fig. 2) [35].

3.1.3. TPR

TPR studies were conducted to determine the relative differences in the reducibility of the catalysts impregnated with different metal loadings. The TPR results of the monometallic catalysts (Pd/HY or Ni/HY) and bimetallic catalysts (Pd-Ni/HY) are presented in Table 1 and Fig. 3. The TPR profile of B₇ featured two reduction peaks at 610 and 780 °C, corresponding to β - and γ -peaks, according to Suzuki and co-workers [39]. The distribution of nickel ions in zeolite Y was discussed by these authors using the TPR technique, and they found that the reducibility of the Ni^{2+} ions occupying sites S_I (α cavity), S_I' (sodalite cavity) and S_{II} or S_{II}' (hexagonal prisms) increased in that order. Thus, according to the reported observations, the hydrogen consumption peaks of B₇ could be attributed to the reduction of Ni^{2+} cations located in sites belonging to sodalite cages (β -peak) and hexagonal prisms (γ -peak), respectively.

Table 1

Physicochemical characteristics of B series catalysts.

Catalyst	Pd content (wt%)	Ni content (wt%)	Surface area (m^2/g)	Porevolume (cm^3/g)	NH_3 -TPD ^a ($\text{mmol}/\text{g}_{\text{cat}}$)			Particle size (nm)	Reduction temperature (°C)
					Weak acidity	Strong acidity	Total acidity		
HY	—	—	367	0.632	0.447 (276)	0.168 (452)	0.615	—	—
B ₁	0.1	—	357	0.625	0.421 (288)	0.142 (468)	0.563	—	180
B ₂	0.1	0.1	332	0.603	0.407 (297)	0.128 (477)	0.535	—	—
B ₃	0.1	0.2	312	0.591	0.384 (312)	0.114 (489)	0.498	—	—
B ₄	0.1	0.3	296	0.588	0.368 (324)	0.102 (496)	0.470	6.08	130, 690
B ₅	0.1	0.4	274	0.561	0.342 (331)	0.094 (508)	0.436	—	—
B ₆	0.1	0.5	252	0.553	0.328 (343)	0.086 (518)	0.414	9.07	110, 670
B ₇	—	0.3	324	0.598	0.312 (328)	0.132 (496)	0.444	—	610, 780

^a The data in parentheses refer to the desorption temperature (°C).

In the TRP profiles of catalysts B₄ and B₆, the above two peaks shifted to much lower temperatures, and the area under the highest temperature Pd peak decreased with increasing Ni contents. Similar results were obtained by Feeley et al. [40] who examined Pd-Ni supported on HY zeolite. The peak shift was attributed to two effects: (1) an enhanced degree of reduction of the nickel species upon interaction with reduced Pd particles present in the supercages, which can dissociatively chemisorb hydrogen, and (2) a Pd-Ni ion-pair formation or nickel ions migration from hexagonal prisms to sodalite cages containing reduced Pd atoms.

Feeley et al. [40] also studied Pd/NaY catalysts calcined at 250 and 550 °C; the catalysts displayed TPR reduction peaks at 150 and 200 °C, respectively. The authors concluded that in the first case, the Pd²⁺ ions were mostly present in the α -cages where they could easily be reduced. For the Pd/NaY sample calcined at the higher temperature, ~70% of the Pd²⁺ ions migrated to the sodalite cages where reduction was more difficult. In the present work, the 0.1 wt% Pd/HY catalyst (B₁), which was calcined at 550 °C, featured only one peak at 180 °C. Thus, the peak could be attributed to the reduction of Pd²⁺ located in the sodalite cages. The temperature difference of 20 °C between the lower peak temperature, corresponding to the reduction of Pd²⁺ ions located in β -positions of HY, and the temperature observed by Feeley et al. [40] for HNaY could likely be related to the redox equilibrium, which was also observed in the reduction of Ni ions in acidic zeolites [41].

3.1.4. XPS

The XPS spectra of the Pd and Ni species in reduced catalysts B₄ and B₆ are shown in Fig. 4. The Pd XPS pattern featured two major peaks regardless of the support and amount of nickel. The peaks with binding energies of 336.4 and 342.0 eV were attributed to the core level Pd 3d_{5/2} and Pd 3d_{3/2} transitions, respectively, indicating the presence of palladium in the metallic state. However, the presence of Pd in higher oxidation states could not be ruled out because of possible peak overlap with that of Al 2p transition of the support [42]. The Ni 2p_{3/2} XPS peaks were observed at 852.3 and 854.0 eV, indicating the presence of metallic nickel and NiO, respectively. B₆ featured a broad peak at ~857.0 eV, indicating the presence of Ni²⁺ and

Fig. 4. XPS spectra of B₄ (1) and B₆ (2) catalysts.

the formation of NiAl₂O₄, from which reduction of Ni²⁺ is very difficult (Ni metal: 852.3 eV; NiO: 853.3 eV; NiAl₂O₄: 857.2 eV in Phi ESCA data book). In an XPS study on the reduction of NiY zeolites by Minchev et al. [43], the latter observed that nickel remained unreduced in the final product. Likewise, an XPS study on Ni-mordenite by Narayanan [44] revealed that the reduction of Ni in mordenite was rather difficult and during reduction, multiple species of nickel formed. Xiao et al. [45] examined the reduction and oxidation behavior of Ni-containing HZSM-5 by XPS and observed the formation of nickel on the surface of the zeolite owing to the interaction between Ni²⁺ and zeolite. Furthermore, the authors observed a surface enrichment in aluminum and nickel. A TRP comparison study between Ni/NaY-zeolite and Ni-Pd/NaY-zeolite by Feeley et al. [40] revealed an enhanced reduction of Ni²⁺ to Ni⁰ by addition of Pd. Likewise, in the present case, the added Pd is likely to favor the reduction of nickel cations within Ni added amounts of 0–0.3 wt% Ni. Above this range, NiO was observed (e.g., 0.5 wt% Ni).

3.1.5. TEM analysis

TEM images of catalysts B₄ and B₆ are shown in Fig. 5. The black dots observed in the support matrix were attributed to the bimetallic (Ni-Pd) particles on the surface of the support. The average size of the particles on each support was determined and is given in Table 1. As observed in Table 1, the average particle size increased with increasing Ni added amounts. In the TPR spectra recorded by Feeley et al. [40], the Ni(8.8)-Pd(3.2)/NaY catalysts displayed a decrease in the Ni reduction temperature with increasing Pd concentrations; the authors attributed this trend to the occurrence of collision among mobile palladium oxide particles by thermal migration and the presence of nickel oxide particles catalytically reduced by pre-reduced Pd particles. The average particle sizes of catalysts B₄ and B₆ were 6.08 and 9.07 nm, respectively. The particles are larger than the pores of the zeolite support (pore size is 7.4 Å: 12MR) and hence may be located mainly outside the pores as reported by Romero et al. [46] for Ni/HZSM-5 catalysts. Furthermore, the authors examined the effect of the Ni loading technique (ion-exchange and impregnation) employed on the particle size of Ni/HZSM-5 by TEM. Large particles always formed on the external surfaces of the zeolite crystals regardless of the metal loading technique employed. Hence, the Ni-Pd particles are likely to grow during reduction as a result of migration of Ni toward originally formed Ni-Pd particles.

Fig. 5. TEM picture of catalysts B₄ (a) and B₆ (b).

3.2. Catalytic studies

Hydroisomerization of *n*-decane was examined over the reduced bifunctional catalysts at a LHSV of 2 h⁻¹ and 200–450 °C in increments of 50 °C. The monobranched isomers, 2-methylnonane (2-MC9), 3-methylnonane (3-MC9), 4-methylnonane (4-MC9), 5-methylnonane (5-MC9), and 3-ethyloctane (3-E8), and dibranched isomers, 2,3-dimethyloctane (2,3-DMC8), 2,4-dimethyloctane (2,4-DMC8), 2,5-dimethyloctane (2,5-DMC8), and 2,6-dimethyloctane (2,6-DMC8), were the major products obtained owing to skeletal rearrangement of the carbon chain; the results are presented in Table 2. Traces of cracked, aromatized, naphthenes and cyclized products were also observed. Products with more than 10 carbons were not observed. Likewise, the lowest carbon numbers (C₁–C₄) were not detected under a wide range of operating conditions, thus ruling out the occurrence of hydrogenolysis reaction of the feed over the metal sites.

3.2.1. Effect of reaction temperature on *n*-decane conversion and isomerization product selectivity

The effect of temperature on *n*-decane conversion over all the catalytic systems prepared is illustrated in Fig. 6. The extent of *n*-decane conversion initially increased with increasing reaction temperatures to up to 400 °C and thereafter decreased. Maximum conversion of *n*-decane over all the catalytic systems was observed at 400 °C. In contrast, the isomerization selectivity of *n*-decane over all the catalytic systems increased to up to 350 °C and then decreased (Fig. 7). When the reaction temperature increased from 350 to 450 °C, more undesirable cracked products were obtained. This result indicates that as tempera-

Table 2

Product distribution of *n*-decane hydroisomerization over B series of catalysts at 350 °C.

Product distribution (wt%)	B ₁	B ₂	B ₃	B ₄	B ₅	B ₆	B ₇
2-MC9	4.8	5.8	6.8	7.4	6.8	5.4	4.1
3-MC9	8.2	9.7	11.5	12.4	11.5	9.2	7.9
4-MC9	4.4	4.8	5.7	6.8	5.9	4.6	2.3
5-MC9	1.7	2.2	3.0	3.9	3.2	2.2	1.4
3-EC8	0.3	0.5	0.7	1.0	0.8	0.4	0.2
Total MBs	19.4	23.0	27.7	31.5	28.2	21.8	15.9
2,3-DMC8	2.6	3.1	3.7	4.5	3.8	2.9	2.2
2,4-DMC8	3.3	4.0	4.9	6.6	5.1	3.5	2.8
2,5-DMC8	2.1	2.7	3.1	4.1	3.2	2.4	1.7
2,6-DMC8	0.6	0.8	1.2	1.4	1.1	0.8	0.4
Total DMs	8.6	10.6	12.9	16.6	13.2	9.6	7.1
Cracked products	4.4	5.1	6.0	6.6	7.1	7.5	8.0
Conversion (wt%)	32.4	38.7	46.6	54.7	48.5	38.9	31.0
Isomerization selectivity (%)	86.4	86.8	87.1	87.9	85.4	80.7	74.2
MBs/DBs	2.3	2.2	2.1	1.9	2.1	2.3	2.2
I/C	6.4	6.6	6.8	7.3	5.8	4.2	2.9
3-MC9/2,4-DMC8	2.5	2.4	2.3	1.9	2.3	2.6	2.8

LHSV = 2 h⁻¹; weight of catalyst = 1 g; flow of H₂ = 20 mL min⁻¹ g⁻¹; time on stream = 1 h; MBs = monobranched isomers; DBs = dibranched isomers; pressure = 1 atm.

Fig. 6. Effect of temperature on *n*-decane conversion over B series catalysts.

ture increases, *n*-decane is more likely to be converted into cracked products rather than the corresponding isomerized products. Y zeolite has a three-dimensional channel structure with an aperture size of 7.4 Å. Thus, the structure of Y zeolite does not thermodynamically favor the formation of dibranched C₁₀ such as 2,3-DMC8 and 2,5-DMC8 at 200 °C or 3EC8 and 2,6-DMC8 even at 300 °C. The formation of dibranched isomers from *n*-octane via monobranched isomers may involve the PCP intermediate as suggested by Zhang et al. [47]. The isomerization selectivity with increasing temperatures reached maximum at 350 °C, which is a typical behavior of the occurrence of consecutive reactions. The rate of hydrocracking, as a secondary reaction, increased rapidly at temperatures above 350 °C over all the prepared catalysts. Specifically, catalyst B₁ displayed a 3.7 wt% *n*-decane conversion and a 54.1% isomerization selectivity at 200 °C. Upon increasing the temperature to 250, 300, 350, and 400 °C, the *n*-decane conversion increased to 7.5, 24.5, 32.4, and 41.1 wt%, with corresponding isomerization selectivities of 72%, 84.1%, 86.4%, and 85.2%, respectively. However, further increases in the reaction temperature from 400 to 450 °C led to a reduced conversion from 41.1 to 34.5 wt%, with a corresponding reduced isomerization selectivity from 85.2% to 78.3%. The steady increase in conversion with

Fig. 7. Effect of temperature on the isomerization selectivity of *n*-decane over B series catalysts.

increasing temperatures (200–400 °C) may be due to activation of the acid sites with temperature and the increase in isomerization selectivity may be attributed to the bifunctional character of the acid sites in the presence of the Pd nanoparticles. The introduction of 0.1 wt% Ni into the catalyst B₁ increased the *n*-decane conversion and isomerization selectivity at all studied temperatures. Over catalyst B₂, *n*-decane conversions of 5.3, 10.2, 30.4, 38.7, and 47.5 wt% were obtained at 200, 250, 300, 350, and 400 °C, respectively. The conversion values were considerably higher than those obtained over catalyst B₁ at the respective temperatures. This result may be due to the activation of acid sites as explained earlier, rather than the introduction of more Ni species. Furthermore, the nanoparticle activity of the bimetallic combination Ni and Pd (both fcc-forming solid solution) may also contribute to the improved conversion values obtained. In contrast, only a small increase in the isomerization selectivity was observed as the catalyst was switched from B₁ to B₂, i.e., 54.1%, 72%, 84.1%, 86.4%, and 85.2% to 60.4%, 74.5%, 84.9%, 86.8%, and 85.5% at 200, 250, 300, 350, and 400 °C, respectively. The small increase in the isomerization values may be attributed to the nanoparticle character of Ni-Pd. However, the selectivity decreased considerably at temperatures above 350 °C over all the catalysts when the metal combination exceeds threshold values. Thus, the decrease in selectivity may be due to either the large particles formed as a result of Ni-Pd combination, which affect the acidity of the support, or the presence of Ni oxide particles that are not completely reduced, hence affecting the acidity on the surface of the support. Among all the catalysts, B₄ (0.3 wt% Ni loaded over 0.1 wt% Pd catalyst) showed high conversion as well as high isomerization selectivity at all temperatures studied. Similar observations were made by Jao et al. [36] in Ni-Pt/MOR and Jordao et al. [48] in Ni-Pt/HUSY that were examined in the isomerization of *n*-hexane. Similar trends, i.e., increases in *n*-decane conversion as well as cracking activity and small increases in isomerization selectivity with increasing reaction temperatures, were observed over all the remaining Pd-, Ni-Pd-, and Ni-loaded catalytic systems, thus indicating the bifunctional nature of the catalysts.

3.2.2. Effect of Ni addition on *n*-decane conversion and isomerization selectivity

The effect of Ni addition on *n*-decane conversion was studied by comparing the *n*-decane conversion over the Ni-containing and Ni free catalysts at a given reaction temperature. The addition of 0.1 wt% Ni over 0.1 wt% Pd/HY enhanced the *n*-decane conversion from 3.7 to 5.3 wt% at 200 °C. At 400 °C, the conversion increased to 41.1–47.5 wt%. Similar increasing trends were observed up to a Ni added amount of 0.3 wt% (over 0.1 wt% Pd) in the HY series catalysts. Further increases in the Ni content (catalysts B₅ and B₆) led to a decreasing trend in *n*-decane conversion at all the temperatures studied. A maximum conversion of 62.1 wt% was obtained over catalyst B₄ at 400 °C. Also, Ni addition up to 0.3 wt% enhanced the isomerization selectivity. Catalyst B₄ displayed the highest isomerization selectivity of 87.9% at 350 °C, which was considerably higher than that observed over catalyst B₁

(86.4%). Further increases in the Ni content in the HY series catalysts (catalyst B₅) led to a significant decrease in isomerization selectivity. The selectivity toward cracking could be controlled at all temperatures studied at Ni added amounts below 0.3 wt%. The increase in *n*-decane conversion, isomerization selectivity, and cracking with increasing Ni added amounts was consistent with the results obtained by Rezgui et al. [26]. In a catalyst with higher metallic site-to-acid site (N_M/N_A) ratios, the diffusion distance between two metallic sites may be shorter when compared with a catalyst with lower N_M/N_A ratios. In the present study, the initial increase in conversion, with a low extent of cracking, observed upon increasing Ni added amounts may be attributed to the formation and growth of catalytically active Ni-Pd bimetallic particles at the nanometer scale as well as an improved balance between the acid sites of the support and bimetallic particles. The high activity and selectivity observed for catalyst B₄ may be attributed to the improved metal-acid sites balance. As discussed above, the TEM studies showed that the average particle size of the bimetallic particles increased with increasing Ni loading. According to the TEM analysis, catalyst B₄ featured an average particle size of 6.08 nm. Furthermore, the XPS spectrum of catalyst B₄ revealed that the Pd and Ni oxides were completely reduced to their respective metallic states. The added Ni species may increase the total number of active metallic sites, i.e., the metallic sites/acid sites ratio may increase to an optimum value toward favoring isomerization reactions. The initial increase in hydroisomerization selectivity and cracking with increasing Ni added contents was attributed to the availability of more metallic sites in the vicinity of the acid sites, thus enabling rapid hydrogenation of the carbenium ions and subsequent desorption as alkanes before the latter underwent cracking reactions. Thus, the probability of cracking the olefinic intermediate during migration from one metallic site to another site was reduced [49]. The decreasing trend in conversion with increasing cracking observed over catalysts with higher Ni contents may be due to the formation of larger bimetallic particles and the presence of unreduced Ni as NiO and NiAl₂O₄, as evidenced by XPS. Catalyst B₆ featured an average particle size of 9.07 nm based on TEM analysis. Similar results were reported by Kuznets et al. [50] in the isomerization of *n*-octane over Pt/HY catalysts, wherein the cracking rate decreased with increasing Pt contents to up to 0.6 wt% and then became independent of Pt loading. Such large bimetallic particles may block the pores of the zeolite and restrict the movement of bulky reaction intermediates. Additionally, the presence of unreduced Ni species, which are inactive in the hydrogenation-dehydrogenation step, may affect the strength of the acid sites, leading to lower activity. Also, the decrease in crystallinity of the supports, as indicated by XRD, likely contributed to the lower activity. The Ni-loaded catalyst (B₇) displayed a considerably lower *n*-decane conversion, with a higher cracking tendency, when compared with catalyst B₄.

3.2.3. Effect of temperature on the selectivity of individual *n*-decane isomers

The effect of temperature on the selectivity of individual *n*-decane isomers was examined over B₄, and the results are

Fig. 8. Effect of temperature on the selectivity of individual *n*-decane isomers over B_4 catalyst.

illustrated in Fig. 8. The selectivity of the monobranched isomers 2-MC9, 3-MC9, 4-MC9, 5-MC9, and 3-EC8 increased with increasing temperatures to up to 300 °C and thereafter decreased over all the catalysts studied. The selectivity of 2-MC9 decreased more than that of 3-MC9. Thus, 3-MC9 formed more readily than 2-MC9. This result was consistent with that observed by Steijns et al. [51] in the hydroisomerization of *n*-dodecane. Additionally, this was a general observation in the hydroisomerization of *n*-alkanes (especially those with ≥ 9 carbon atoms). This result is best explained by the occurrence of a PCP mechanism involved in the isomerization reaction [52]. The formation of 3-EC8 over the catalysts, even at very low conversions, could not be explained by the occurrence of a protonated cyclopropane mechanism. The primary formation of 3-EC8 can most likely be explained by the participation of a B isomerization reaction of protonated cyclobutane intermediates (PCB) as proposed by Martens et al. [53]. The selectivity of the dibranched isomers 2,3-DMC8, 2,4-DMC8, 2,5-DMC8, and 2,6-DMC8 increased with increasing temperatures. Among these dibranched isomers, 2,4-DMC8 featured the highest selectivity. The present data indicate that the predominate dibranched isomers were those featuring distant methyl groups (2,3-DMC8 and 2,4-DMC8). Similarly to the first branching, the formation of less bulky PCP intermediates involved in the second branching is strongly favored, thus explaining the low selectivities for dibranched isomers containing methyl groups within close proximities to each other [54]. According to Lucas et al. [55], the formation of the dibranched decane isomer can be attributed to the formation of a bulkier transition state and intermediates of isomers, such as 2,2-dimethyloctane and 3,3-dimethyloctane, with two branches on the same carbon of the main chain. Their formation is favored in zeolites without steric hindrance for the diffusion of products. It should be noted that for zeolites with relatively large pores, such as beta zeolites, the presence of these isomers is more predominant. The increase in the extent of formation of dibranched isomers with increasing temperatures, as well as conversion, indicates that the dibranched isomers are secondary products formed from primary monobranched isomers by formation of a proto-

nated cyclopropane intermediate. Similar results have been reported in our previous studies [33–35]. In contrast, tri-branched isomers were not detected regardless of the catalyst investigated in this work. This result was attributed to the relatively high temperatures employed, which do not favor the thermodynamic formation of tribranched isomers. Moreover, fast cracking of the latter hydrocarbons was responsible for the absence of tribranched isomers in the final products [47]. The selectivity of the monobranched isomers was higher than that of the dibranched isomers. The earlier observations indicated that the pore structure, size, and kinetic diameter of the reactants, products, and intermediates contributed to the different selectivities of the dibranched isomers. Zeolite Y has a faujasite structure with a three-dimensional channel system of 12 MR (pore size: 7.4 Å) intersections [56]. The kinetic diameters of *n*-decane, monobranched, and dibranched isomers increased in the order of *n*-decane < monobranched isomers < dibranched isomers. Hence, the formation of the dibranched isomers may be sterically hindered by the presence of metallic particles in the pores.

3.2.4. Effect of temperature on the MB_s/DB_s ratio

The effect of temperature on the ratios of the octane isomers over the catalysts is illustrated in Fig. 9. The ratio of 3-MC9/2,4-DMC8 decreased with increasing reaction temperatures to up to 400 °C. It is generally considered that the branching of olefins occurs through the protonated cyclopropane intermediate as per the comprehensive description of carbenium ion rearrangement and cleavage by Weitkamp [52]. From the point of view of PCP mechanism, the isomerization of monobranched to dibranched decanes proceeds through secondary and tertiary carbocations, and therefore it should be thermodynamically favorable. The 3-MC9/2,4-DMC8 ratio decreased with increasing temperatures and Ni contents up to the threshold value. The increase in the extent of dibranched decane formation with increasing Ni contents as well as temperatures indicates that the addition of Ni and higher reaction temperatures favors the protonated cyclopropane intermediate mechanism, which is considered to be slower than the 1,2-alkyl hydride shift mechanism, which leads to the formation of

Fig. 9. Effect of Ni addition on the 3-MC9/2,4-DMC8 ratio over B series catalysts at different temperatures.

monobranched isomers. The increased extent in the occurrence of the PCP mechanism can be attributed to a better balance between the formed metal particles and the acid sites. Catalysts featuring large metal particles do not favor the PCP mechanism as the large particle size affects the development of optimum metal–acid site balance. The unreduced Ni (as observed in the XPS analysis), although not active in the dehydrogenation–hydrogenation step, may play a role in the isomerization of *n*-decane as well as the ratio of the isomers formed. The decrease in the 3-MC9/2,4-DMC8 ratio with increasing Ni contents indicates that Ni addition facilitates the formation of the dibranched isomers through a PCP intermediate mechanism and suppresses the 1,2-alkyl hydride shift reaction, which typically leads to the formation of 3-MC9 from 2-MC9. Hence, the *n*-decane isomerization is considered to proceed via a carbenium ion rearrangement and cleavage mechanism. According to the comprehensive description of rules for carbenium ion rearrangement and cleavage given by Brouwer [57], carbenium ion isomerizations, which lead to a change in the degree of branching, proceed through a protonated cyclopropane PCP ring intermediate formation mechanism.

3.2.5. Effect of Ni addition on isomerization/cracking (I/C) ratio

The I/C ratio of a catalyst is an indication of its suitability for isomerization reactions. Excellent isomerization catalysts have very high I/C ratios. As observed in Fig. 10, the I/C ratio increased with increasing Ni added contents to up to 0.3 wt% (B₄ catalyst). Further increases in the Ni content lowered the I/C ratio, indicating the higher cracking activity of larger bimetallic particles. Overall, the catalytic system I/C ratio decreased with increasing temperatures, indicating that higher temperatures favor cracking.

3.2.6. Effect of reaction time

The performance of the catalyst was further examined over a reaction period of 15 h at 400 °C. The results are shown in Fig. 11. All catalysts showed large decreases in the conversion with increasing reaction times up to 5 h, after which small de-

Fig. 10. Effect of Ni addition on the I/C ratio over B series catalysts at different temperatures.

Fig. 11. Time-on-stream behavior of *n*-decane hydroisomerization over B series catalysts.

creases were observed with increasing reaction times up to 15 h. Among all catalysts, B₄ displayed the lowest reduction. In contrast, B₁ and B₇ showed the highest reduction in activity. The higher (sustained) performance of B₄ can be explained in terms of the formation of catalytically active bimetallic particles and better balance between the metal and acid sites. The decrease in activity of the catalysts can be related to the formation of coke, which can block the active sites of the catalysts.

To understand the role of the noble metal Pd in HY zeolite on the performance of the catalysts, the reaction was conducted under optimized conditions (LHSV = 2 h⁻¹; weight of catalyst = 1 g; H₂ flow = 20 mL min⁻¹ g⁻¹; reaction time = 1 h; pressure = 1 atm; reaction temperature = 350 °C) using HY zeolite (without metal loading) as a catalyst. HY achieved a conversion of 12.8 wt% and an isomerization selectivity of 38.4% and generated a high amount of cracked products (21.1%). In contrast, B₄ catalyst, when operating under optimized conditions, achieved a conversion of 54.7 wt%, with a corresponding isomerization selectivity of 87.9% and a low amount of cracked products (6.6%). These performance values were considerably better than those achieved by HY zeolite. Based on these results, it can be concluded that the presence of noble metal catalysts plays a vital role in achieving high conversion and product selectivity.

To examine the recyclability of the catalysts, the reaction was performed for five successive cycles under the aforementioned optimized conditions over B₄. After each cycle, the catalyst was regenerated at 500 °C in air. In general, both the conversion and selectivity decreased after each cycle; however, the reduction was not significant (Table 3).

Table 3
Recyclability of the B₄ catalyst.

No. of cycles	Conversion (wt%)	Selectivity (%)
Fresh catalyst	54.7	87.9
1st cycle	54.4	87.5
2nd cycle	54.1	87.2
3rd cycle	53.8	86.9
4th cycle	53.6	86.6
5th cycle	53.4	86.4

4. Conclusions

Y zeolite was loaded with Pd and Ni at varying amounts using an impregnation method. The resulting products were characterized and examined as catalysts in the hydroisomerization of *n*-decane. The XRD results confirmed the good crystallinity of the commercial Y zeolite support. Upon loading with Ni at increasing amounts, the structure and crystallinity of the resulting metal-loaded zeolites decreased. The TEM analysis revealed the formation of bimetallic (Ni-Pd) nanoparticles. The ESCA study revealed complete reduction of Ni up to a Ni loading of 0.3 wt% over 0.1 wt% Pd-loaded HY. The TPR results showed a decrease in the Pd reduction temperature with increasing Ni added amounts. The acidity measurements by TPDA indicated that some of the acid sites were occupied by the Ni species. Owing to the excellent metal–acid site balance between the bimetallic particles and acid sites of the support, catalyst B₄ showed higher activity, dibranched isomer selectivity, and performance sustainability in the hydroisomerization of *n*-decane when compared with the remaining catalysts.

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Graphical Abstract

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Effect of metal content on the activity and product selectivity of *n*-decane hydroisomerization over Ni-Pd/HY zeolite

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Zeolite-Y was impregnated with 0.1 wt% Pd and 0.1 to 0.5 wt% Ni. The synthesized catalyst shows an enhanced activity, dibranched isomers selectivity and sustainability of the catalysts in *n*-decane hydroisomerization.

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金属含量对Ni-Pd/H-Y上正癸烷加氢异构化反应活性和产物选择性的影响

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摘要: 在Y分子筛上浸渍0.1 wt% Pd和0.1–0.5 wt% Ni, 用X射线衍射表征了该催化剂的结晶度, 用透射电镜测得平均金属粒径. 催化剂中Pd和Ni的化学态用X射线光电子能谱测定, 其酸性则用氨-程序升温脱附进行了表征, 发现一些酸位被Ni²⁺离子交换. 采用程序升温还原表征了HY分子筛负载的Pd, Ni和Pd-Ni催化剂的还原性能. 正癸烷加氢异构化反应在200–450 °C和1 atm条件下进行. 结果发现, 当0.1 wt% Pd/HY中Ni添加量增至0.3 wt%时, 正癸烷转化率和异构化选择性增加. 单支链和双支链异构体选择性的增加表明该反应遵循质子化环丙烷中间体机理. Ni添加量超过阈值导致活性和异构化选择性急剧下降. 综上所述, 双金属催化剂更有利于选择性生成双支链异构体, 其辛烷值更高.

关键词: 加氢异构化; 正癸烷; Y分子筛; 钯; 浸渍方法

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