

## Nickel Hydrogenation Composite Catalysts Modified by Zirconium in Competitive Benzene Hydrogenation: Effect of Modifiers

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A co-impregnation method was applied to the Ni/Zr-HMS/HZSM-5 catalyst (with various amounts of zirconium) during the hydrogenation of benzene. The physicochemical properties of the prepared nickel catalyst were characterized using X-ray diffraction, X-ray fluorescence, Fourier transform infrared spectroscopy, ultraviolet-visible diffuse reflectance spectroscopy, temperature-programmed desorption of ammonia, H<sub>2</sub> chemisorption, N<sub>2</sub> adsorption-desorption, and thermogravimetric analysis. The catalytic performance was assessed on a fixed-bed reactor (reaction temperature between 130 °C and 190 °C). The results indicated that the nickel catalyst with Si/Zr = 35 exhibited better catalytic performance and stability than others, so providing a better selectivity in a long-term performance.

**Keywords:** Impregnation, Hydrogenation, Conversion, Selectivity, Stability

### INTRODUCTION

In the recent decades, decreasing the benzene amount in gasoline has been a great challenge for the refineries due to the severe environmental principles on fossil fuels [1,2]. Because of the carcinogenic properties of benzene, the extent of this substance in reformat gasoline should be reduced to produce clean fuel for the environment. A large portion (near 80%) of benzene in gasoline is created at the catalytic reforming phase. A proposed method for decreasing the extent of benzene is a fractionation of gasoline and hydrogenation of the fraction with advanced benzene content. Finally, these two fractions are mixed to produce a fuel with less environmental risks and a high octane number [3-5].

In many studies performed, the main focus has been on the catalyst synthesis method and less on the practical aspect of the hydrogenation reaction of benzene to cyclohexane. For example, Liao *et al.* [6] studied catalytic synthesis of Ru-La supported on MCM-41 and

polydopamine-modified MCM-41 by double solvent impregnation method and eventually applied them to the hydrogenation reaction of benzene to cyclohexene. Le *et al.* [7] focused on the production of high nickel content-based silica catalysts by the precipitation method. In the hydrogenation process of benzene, they concluded that the wet impregnation method is better than others. Li *et al.* [8] also investigated the morphology effect of the Pd/CeO<sub>2</sub> catalyst on this reaction and found that the Nano rod catalyst had a superior performance.

In available papers, supported metals are the most general catalysts for the hydrogenation reaction of benzene. Metals such as Pt, Pd, Ni, Ru, Ir and Fe, and supports such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and TiO<sub>2</sub> have been considered by different research groups [9-14]. Nickel, being low-cost than noble metals and representing high activity, has been studied widely in the literature and currently is used in industry [12,15,16]. The various factors affecting the catalyst activity in the hydrogenation reaction include the nature of support, dispersion of metal on the support surface and reduction of active sites. Methods used for producing and pre-treating of catalyst can affect these factors [17,18].

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Based on the literature, the activity of acidic catalysts is high in the hydrogenation reaction due to the presence of the more active sites for hydrogenation. In this kind of catalyst, aromatic compounds can be adsorbed onto the acidic sites of the support and react with spilled-over hydrogen from the metal [19-21].

Most research activities have centralized on pure benzene hydrogenation and only a partial number of articles have used a mixture of hydrocarbons [15,22,23]. Thus, the competition of compounds for adsorption on the catalyst and the following reaction have not been studied thoroughly. A non-selective catalyst can cause the hydrogenation of various aromatic compounds in gasoline, which causes the octane number to drop. Accordingly, the use of selective catalysts to benzene is essential.

In this investigation, Ni-Zr was supported on hexagonal mesoporous silica (HMS) with H form of Zeolite Socony Mobil-5 (HMS/HZSM-5) via a co-impregnation method to examine the synergic effect of the metals in the bimetallic catalyst. Numerous Si/Zr ratios were applied in this study, and the catalysts were assessed by the selectivity of benzene hydrogenation in a mixed solution of aromatics. The purpose of this paper is to enhance the acidity of the support and find a proper Si/Zr ratio in our catalysts. The physicochemical properties of the organized catalysts were described by different techniques and reaction kinetics and the effects of temperature and residence time on the activity and stability of the catalysts were also studied.

## EXPERIMENTAL

### Catalyst Synthesis

HMS/HZSM-5 alumina-silicate was synthesized using our reported method [24] according to Schematic 1. For doing so, 1 g of HZSM-5 (Zeolyst International; Si/Al = 14) was added to various amounts of ethanol, tetraethyl orthosilicate, dodecyl amine, hydrochloric acid (1 M), and distilled water. The obtained product was filtered and dried at 110 °C for 12 h and calcined during 6 h on air with a heating rate of 1 °C min<sup>-1</sup> to 600 °C.

Nickel and zirconium metals were loaded over supports by the co-impregnation method with special amounts of nickel(II) nitrate hexahydrate, and zirconyl(IV) nitrate solutions. The Ni loadings were selected as 25 wt% and the

Zr loadings were different. After evaporation of water, these catalysts were dried at 110 °C on air for 12 h and calcined at 300 °C for 4 h. The resulted Ni-Zr(x)-HZSM-5/HMS catalysts were labeled NiZr(x)-ZH, where x is the nominal Si/Zr ratios equal to 20, 35 and 45.

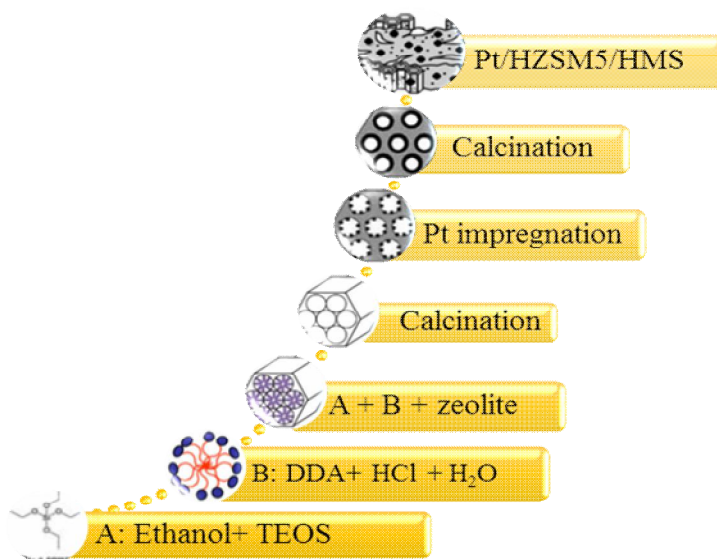
### Catalyst Characterization

X-ray fluorescence was recorded with an XRF-8410 Rh apparatus and a voltage of 60 kV to measure silicon to zirconium ratios and metal contents. The X-ray powder diffraction patterns were recorded on an X-PERT diffractometer using nickel-filtered Cu k<sub>α</sub> radiation at 45 kV and 50 mA. The intensity data were collected over these conditions: 2θ = 0-80°, step size = 0.06° and step time = 1 s. The tablets of the mixed catalysts and KBr were characterized in the wavenumber range of 400-4000 cm<sup>-1</sup> by FT-IR spectroscopy using the BOMEM FTIR spectrophotometer model Arid-Zone MB series.

The amounts of acidic sites were measured by ammonia-TPD on a semiautomatic Micromeritics TPD/TPR 2900 apparatus connected to a computer. The measurement conditions are as follows: mass of each catalyst: 0.2 g, T = 600 °C, heating rate = 10 °C min<sup>-1</sup>, helium flow = 40 ml min<sup>-1</sup>, and time = 1 h. After cooling to 100 °C, TPD experiments were achieved in a 10 vol% stream of NH<sub>3</sub>-He flow until the acid sites of the catalysts were filled with NH<sub>3</sub>. Then, desorption profiles were recorded with a 10 °C min<sup>-1</sup> rate up to 800 °C.

The BET isotherms were made to measure the surface area of catalysts using the ASAP-2010 micromeritics (USA) device. Before the analysis, outgassing the calcined catalysts was done at 300 °C for 3 h. The volume of the adsorbed monolayer (V<sub>p</sub>) and the specific surface area (S<sub>BET</sub>) were calculated by taking the BET equation and also the average pore diameter (d<sub>p</sub>) was calculated by the Barret-Joyner-Halenda method.

UV-Vis DRS was recorded in 200–800 nm at room temperature using a Shimadzu UV-2100 UV-Vis spectrophotometer. Hydrogen-TPR of the samples was done using a TPD/TPR analyzer (2900 Micromeritics) equipped with a TCD to evaluate the dispersion of the metals. Before the analysis, approximately 0.2 g of the catalysts were reduced at 450 °C for 1 h and erased with the argon at 500 °C for 1 h. The TPR runs were carried out on pure H<sub>2</sub>



*Schematic 1.* The trend of synthesizing catalyst

with a flow rate of  $14 \text{ ml min}^{-1}$  until no further adsorbed hydrogen remained on the surface of catalysts. The hydrogen utilization was admeasured quantitatively by a thermal conductivity detector.

The amounts of coke depositions were calculated by thermogravimetric and differential thermal analysis (TG/DTA) with a STA503 M medium. For this measurement, 20 mg of each sample was treated at 25 to  $800 \text{ }^\circ\text{C}$  with 5 vol% of a gaseous mixture of oxygen and nitrogen with a  $60 \text{ ml min}^{-1}$  flow rate.

### Catalytic Activity and Stability Tests

Hydrogenation of aromatic compounds was conducted in a continuous fixed-bed Pyrex reactor connected to a gas chromatograph and a controller. Each catalyst (1 g) was poured into the reactor alone. To pre-reduce the metallic function and activate the catalysts, each catalyst was heated to  $450 \text{ }^\circ\text{C}$  for 2 h in an  $\text{H}_2$  stream at atmospheric pressure. The mixture of some aromatics as benzene (6 vol%), toluene (8 vol%), and xylene (8 vol%) dissolved in n-heptane was used as a model for initial feed. This mixture with hydrogen was injected into the reactor with  $2 \text{ ml h}^{-1}$  and  $40 \text{ ml min}^{-1}$  flow rates, respectively. The conditions for this catalytic study are as follows:  $T = 130\text{-}190 \text{ }^\circ\text{C}$  and  $P = 1 \text{ atm}$ .

Catalytic activity was calculated in terms of conversion

which is defined as a fraction of the reacted aromatics. The following equation was also used as an overall aromatic conversion ( $Ov_{conv}(\%)$ ) for a mixed solution:

$$Ov_{conv}(\%) = (m_{Bz} \cdot conv_{Bz} + m_{Tu} \cdot conv_{Tu} + m_{Xy} \cdot conv_{Xy}) \times 100 \quad (1)$$

where  $m$  and  $conv_x$  are the molar ratio and conversion in benzene/toluene/xylene mixture, respectively. The following equation was used for calculating selectivity to each product:

$$S_{Bz}(\%) = \frac{m_{Bz} \cdot conv_{Bz}}{Ov_{conv}} \times 100 \quad (2)$$

To study the coke deposition and catalyst deactivation, the influence of acidity, and also, nickel and zirconium amounts on the catalytic performances were examined by the stability test. The operating conditions are similar to the activity performed at a selected constant temperature ( $150 \text{ }^\circ\text{C}$  according to the best benzene selectivity). Each catalyst was examined for 10 h underflow. The products were also identified with an on-line gas chromatograph.

### Kinetic Studies

NiZr(x)-ZH catalysts were studied during kinetic tests.

In this study, the reaction order and activation energy were measured for benzene hydrogenation. The reaction orders were computed for the benzene concentration (2-8 vol%) and hydrogen pressure (2.6-5.9 Pa) at 130-190 °C temperature range. The products were analyzed by gas chromatography at a fixed interval of time.

The test was carried out in lower conversion conditions (<10%) to produce a linear Arrhenius plot. The apparent activation energies ( $E_{app}^{act}$ ) were obtained from the logarithmic form of the Arrhenius equation at a lower 10% conversion to reach a linear plot.

$$\ln k = \ln A - \frac{E_{app}^{act}}{RT} \quad (3)$$

In this equation,  $k$  is the rate constant and  $A$  is a pre-exponential factor.

It is worth mentioning that the reaction rate was defined as follows;

$$r \left( \frac{\text{mol}}{\text{g} \cdot \text{s}} \right) = \frac{Bz \text{ flow rate} \left( \frac{\text{ml}}{\text{s}} \right) \cdot Bz \text{ density} \left( \frac{\text{g}}{\text{ml}} \right) \cdot \text{Conv} (\%)}{Bz \text{ molar weight} \left( \frac{\text{g}}{\text{mol}} \right) \cdot \text{Weight of catalyst} (\text{g}) \cdot \text{Im pregnated metal} (\text{wt}\%)} \quad (4)$$

To measure the reaction orders, the method described in our previous work has been used [25]. These reaction orders were measured by the following empirical kinetic equation:

$$r \left( \frac{\text{mol}}{\text{g} \cdot \text{s}} \right) = k P_{H_2}^n P_{Bz}^m \quad (5)$$

where  $n$  and  $m$  are the partial orders of hydrogen and benzene, respectively, and  $k$  is the rate constant.

## RESULTS AND DISCUSSION

### Catalyst Characterization

The metal contents of NiZr(x)-ZH calcined catalysts were examined by the XRF method. The obtained results show the near contents to the desired amounts (Table 1). The powder XRD patterns (Fig. 1) of calcined NiZr(x)-ZH with 25 wt% of nickel and different Si/Zr ratios (20, 35 and 45 wt%) reveal strong characteristic peaks of the HMS

framework at a low angle (2.3°). ZSM-5 phase's peaks are at 6-11° and 22-25° and the broad diffraction line observed between 20° and 30° in the spectra are related to the amorphous part of HMS [25]. Increasing the amount of Zr increases the intensity of the HMS peak and reduces its width, indicating that increasing lattice disorder is caused by the insertion of zirconium. The XRD peaks of Ni phase (NiO) are seen at  $2\theta = 37.2^\circ, 43.2^\circ, 62.7^\circ, 75.2^\circ$  and  $79.4^\circ$  angles [26]. Additionally, no characteristic peaks of Zr are visible, indicating that zirconium was dispersed homogeneously without the formation of the agglomerated zirconium.

The FT-IR spectra of these bimetallic catalysts at room temperature (Fig. 2) demonstrate the bands of physisorbed water at around 1600 and 3400  $\text{cm}^{-1}$ . The characteristic bands of HMS, due to the asymmetric stretching and bending modes of  $\equiv\text{Si-O-Si}\equiv$ , are seen at 1200, 1100 and 440  $\text{cm}^{-1}$ . The bands of the ZSM-5 part of these composite catalysts observed at nearby 1000, 790 and 540  $\text{cm}^{-1}$  are assigned to the asymmetric and symmetric stretching vibration bands of HZSM-5 components.

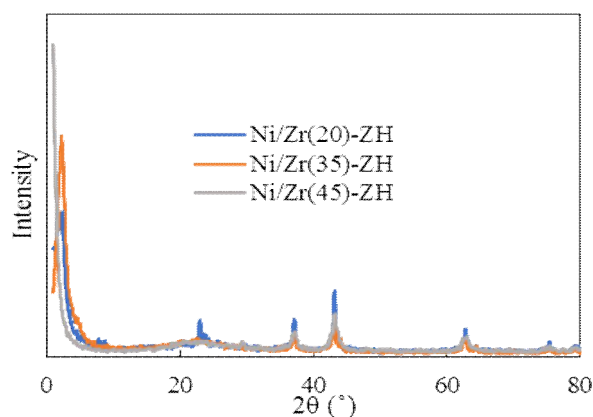
The chemical states of Ni and Zr particles over HZSM5/HMS composite were recognized with diffuse reflectance UV-Vis spectra (UV-Vis DRS). The spectra of Ni-Zr-supported catalysts were collected under environmental conditions. The position of the absorption bands exposures the coordination and aggregation of the metal oxides. The bands around 250 nm and 200 nm are recognized to an absorption associated with a charge transfer transition of  $\text{O}^{2-}\text{-Ni}^{2+}$  and  $\text{O}^{2-}\text{-Zr}^{4+}$  for NiO and  $\text{ZrO}_2$  species, respectively. A shoulder observed above 300 nm is attributed to the d-d transitions of  $\text{Ni}^{2+}$  and probably the bulk  $\text{ZrO}_2$  phase and part of the tetrahedrally coordinated zirconium species. The intensities variations of the bands of these catalysts' spectra may be due to the differences in the interaction strength of species and their population on the supports.

Nitrogen physisorption isotherms were used to conclude the textural properties of the prepared materials. According to the International Union of Pure and Applied Chemistry (IUPAC) classification, the NiZr(x)-ZH catalysts follow isotherm type IV with H1 characteristic hysteresis loops of mesoporous materials with identical tubular pores. Two

**Table 1.** Physicochemical Properties of the Named Catalysts

Catalyst	NiZr(20)-ZH	NiZr(35)-ZH	NiZr(45)-ZH
Surface properties			
$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	701	742	798
$V_p$ ( $\text{cm}^3 \text{g}^{-1}$ )	0.42	0.45	0.52
$S_{\text{micro}}$ ( $\text{m}^2 \text{g}^{-1}$ )	125	134	145
$V_{\text{micro-p}}$ ( $\text{cm}^3 \text{g}^{-1}$ )	0.15	0.16	0.18
$d_p$ (nm)	2.39	2.43	2.61
Acidic properties			
Weak acid <sup>a</sup>	0.344	0.335	0.122
Strong acid <sup>b</sup>	0.247	0.244	0.091
$M_d$ (%) <sup>c</sup>	50.2	52.3	36.6
Si/Zr <sup>d</sup>	18.3	33.8	43.5

<sup>a</sup>Below 300 °C vs. mmol of  $\text{NH}_3$  (g), <sup>b</sup>above 460 °C vs. mmol of  $\text{NH}_3$  (g), <sup>c</sup>using  $\text{H}_2$  chemisorption, <sup>d</sup>by XRF.

**Fig. 1.** The XRD patterns of the named catalysts.

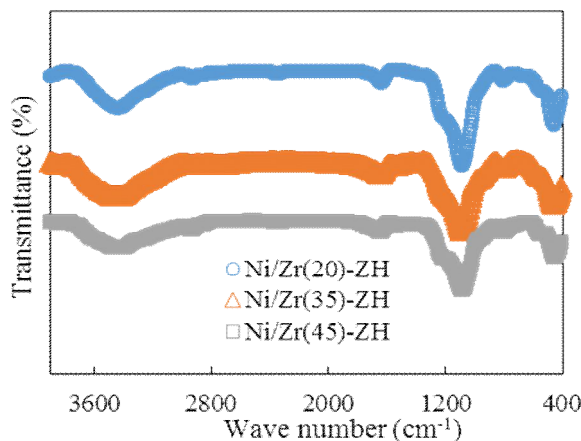
steps of capillary condensation represented the particle size are ostensible in these isotherms.

The first step is related to the intraparticle mesoporosity inside the catalysts at  $P/P_0 = 0.3$ , and the second, interparticle textural porosity at  $P/P_0 = 0.9$  with a small hysteresis loop; smaller particle size demand higher partial

pressure. The BET surface area of the synthesized materials changes as follows:

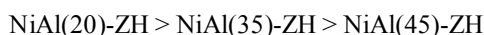
$$\text{NiZr(45)-ZH} > \text{NiZr(35)-ZH} > \text{NiZr(20)-ZH}$$

Textural characterization results ( $S_{\text{BET}}$ ,  $V_p$ , and  $d_p$ ) for the



**Fig. 2.** The FT-IR spectra for the synthesized catalysts.

catalysts are listed in Table 1. It can be concluded from the results that increase in the Si/Zr ratio results in an increment of textural characteristics of these catalysts. By increasing the Zr amounts, a decrease in the pore volume, pore diameter, and surface area are observed. The acidity distributions on the surface of the catalysts are also listed in Table 1. The amounts of weak and strong acids for these catalysts are in the range of 0.12-0.34 and 0.09-0.25 mmol  $g_{cat}^{-1}$ , respectively. Two desorption peaks in the temperature region of 100-600 °C, interpreted as the desorption peaks of the weak and strong acids, were observed for these catalysts. The trend of overall acidity is as follows:



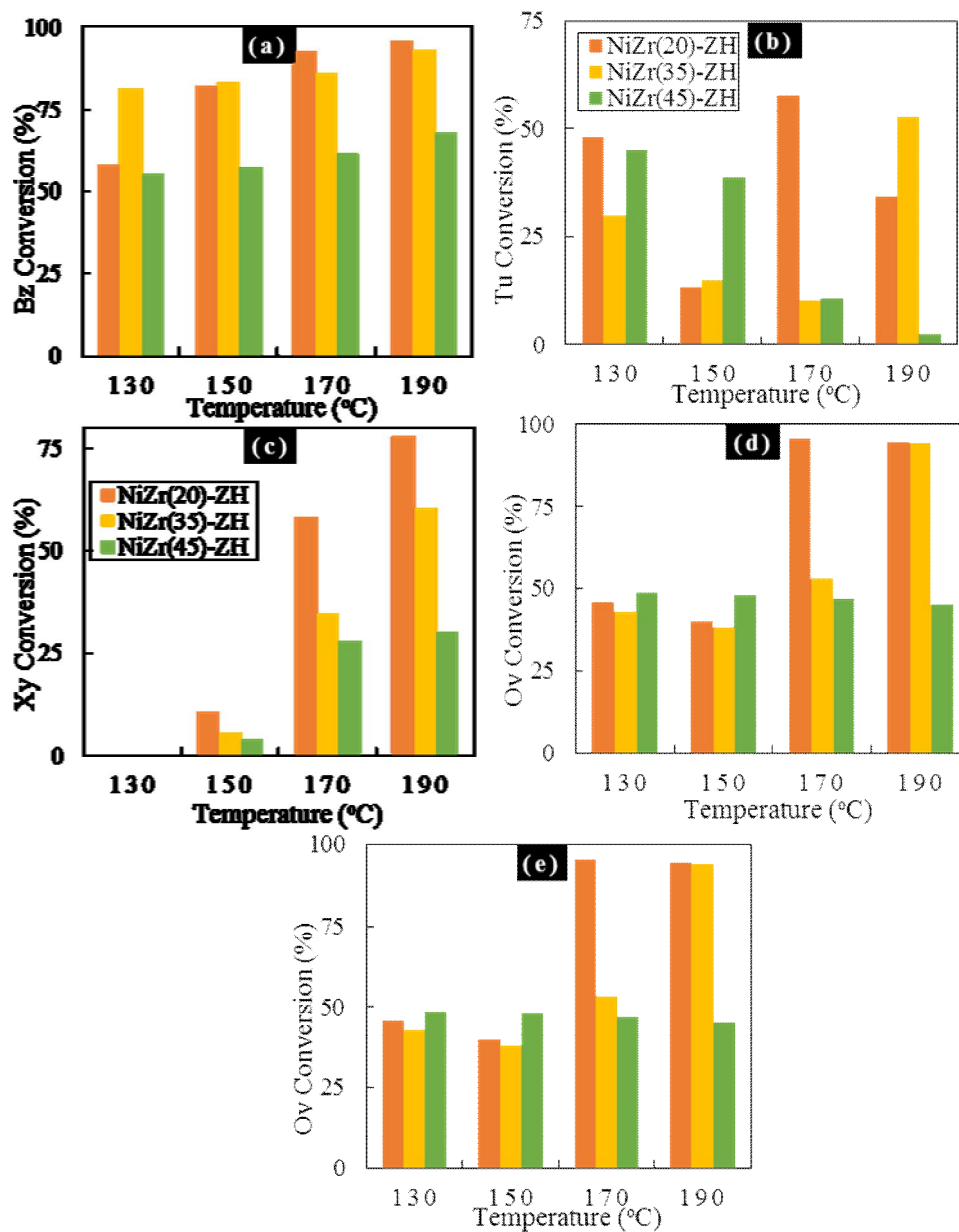
### Catalytic Performance

The catalytic activity of these composite catalysts is demonstrated as benzene (Bz), toluene (Tu), and xylene (Xy) (pure and mixture) conversions in Fig. 3.

These aromatic compounds were applied as a model for the hydrogenation reaction of gasoline. Cyclohexane, methylcyclohexane, and dimethylcyclohexane as the only products were recognized. These obtained products indicate the total hydrogenation of the aromatics used in the catalysts. Figure 3 presents Bz, Tu, and Xy conversions at pure solutions and also overall conversion and Bz

selectivity at a ternary mixture in 1 h on stream over the catalysts. Increasing the temperature resulted in increased Bz and Xy hydrogenation and decreased Tu hydrogenation. The NiZr(20)-ZH catalyst has the best conversion for Bz and Xy nearly in all temperatures, but none of the catalysts confirmed superiority in Tu conversion. At 190 °C, Bz conversion for all catalysts reached the highest value. The NiZr(45)-ZH catalyst had the lowest Bz conversion (57%) at 150 °C. The same trend is noticeable in Xy conversion. At 130 °C no reaction occurred and by increasing temperature, conversions increased. NiZr(20)-ZH was the best catalyst for Xy hydrogenation. The Tu conversion does not follow a linear trend and has the highest amounts at 130 °C. Regarding overall conversion, NiZr(20)-ZH catalyst at 170 °C achieved the highest conversion. NiZr(20)-ZH and NiZr(35)-ZH showed higher conversions above 170 °C, while NiZr(45)-ZH was not affected by the temperature.

As the Bz selectivity of the catalysts in the ternary solution, NiZr(35)-ZH shows the best Bz selectivity at 150 °C. NiZr(20)-ZH and NiZr(35)-ZH reveal an increase in selectivity from 130 to 150 °C, but their selectivity decreases when temperature further rises. It can be deduced from these results that the best temperature for the selective performance is 150 °C. The temperature did not have a significant effect on NiZr(45)-ZH. Briefly, the NiZr(35)-ZH catalyst had a Bz conversion of 83% and the highest Bz selectivity (79%) compared to other catalysts at 150 °C. This confirms that NiZr(35)-ZH catalyst displayed high



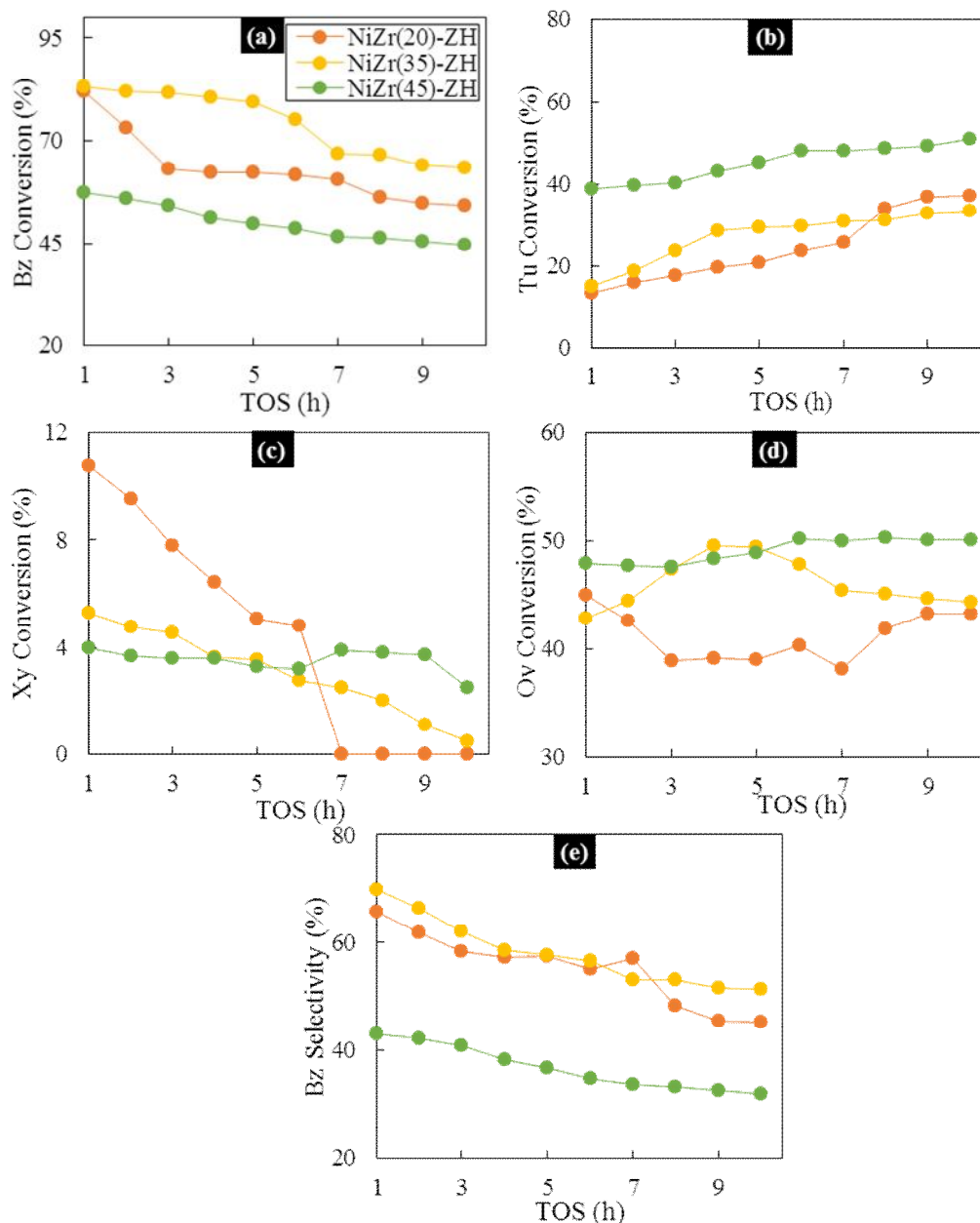
**Fig. 3.** The effect of temperature on (a) benzene, (b) toluene, (c) xylene, and (d) overall conversions, and also (e) benzene selectivity.

activity and selectivity for benzene at low temperatures.

The stability of the produced catalysts was measured during a 10 h period on stream at 150 °C (Fig. 4). It was detected in all catalysts that the Bz and Xy conversions diminished and Tu conversion increased during this period. Even though the overall conversion was almost constant.

The lowest and highest decreases in Bz conversion were observed for NiZr(45)-ZH and NiZr(20)-ZH, respectively. The best Bz selectivity (above 52%) after 10 h was observed for NiZr(35)-ZH, signifying good stability of this catalyst compared to others.

The rapid formation of coke could be the cause of loss



**Fig. 4.** The effect of time on stream of (a) benzene, (b) toluene, (c) xylene and (d) overall conversions, and also (e) benzene selectivity over NiZr(x)-ZH catalysts at 150 °C.

of activity in the early hours of the reaction. To measure the deposition of coke on the catalyst surface, TGA analysis was used. According to the results, 2.2 wt%, 0.9 wt% and 0.2 wt% of coke were deposited on NiZr(20)-ZH, NiZr(35)-ZH, and NiZr(45)-ZH catalysts, respectively.

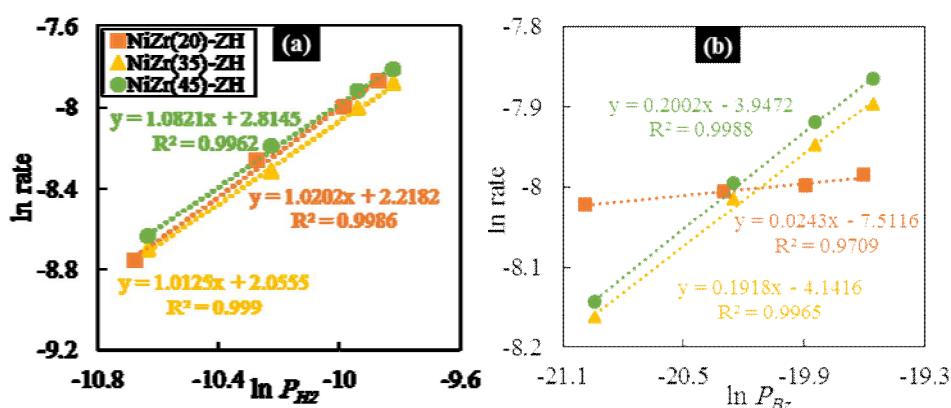
### Kinetic Studies

Table 2 summed up the activation energies and the reaction orders of benzene and hydrogen. Likewise, the dependence of the reaction rate on the partial pressure of hydrogen and benzene is demonstrated in Fig. 5. The



**Table 2.** Kinetic Parameters for Benzene Hydrogenation

Catalyst	NiZr(20)-ZH		NiZr(35)-ZH		NiZr(45)-ZH	
	$n_{H_2}$	$m_{Bz}$	$n_{H_2}$	$m_{Bz}$	$n_{H_2}$	$m_{Bz}$
T = 130 °C	1.069	0.021	1.009	0.174	1.000	0.180
T = 150 °C	1.071	0.021	1.012	0.191	1.009	0.198
T = 170 °C	1.082	0.024	1.012	0.199	1.020	0.200
T = 190 °C	1.121	0.032	1.013	0.204	1.060	0.230
$E_{app}^{act}$ (kJ mol <sup>-1</sup> )	30.47		18.58		40.05	

**Fig. 5.** Double-log plots of the benzene hydrogenation rate *versus* the partial pressures of (a) hydrogen and (b) benzene at 170 °C for the named catalysts.

reaction rate increases by raising hydrogen partial pressure, but it does not follow a particular development by altering the benzene partial pressure. The measured orders at constant temperature on bimetallic catalysts NiZr(x)-ZH (x = 20, 35 and 45) for benzene were 0.021-0.032, 0.174 to 0.204 and 0.180 to 0.230, respectively, and for hydrogen, the reaction orders were 1.069-1.121, 1.009-1.013 and 1.000-1.060, respectively (Table 2).

These results are in relative agreement to the literature [11]. As can be seen in this table, the reaction orders of H<sub>2</sub> and benzene increase with reaction temperature, probably due to a considerable decrease in the coverage of each reactant.

The results of the apparent activation energies were in

good agreement with the ones reported in the literature for supported nickel catalysts (Table 2) [27]. For this reaction, the calculated activation energies from the Arrhenius plot were 30.47, 18.58 and 40.05 kJ mol<sup>-1</sup> for the prepared catalysts, respectively. The kinetic studies of the activation energies indicate that the benzene hydrogenation carried out on NiZr(35)-ZH (18.58 kJ mol<sup>-1</sup>) is easier and quicker than that in the other prepared catalysts.

## CONCLUSIONS

The hydrogenation of benzene, toluene, and xylene as a model reaction for gasoline hydrogenation was investigated over HMS-HZSM5 supported Ni-Zr bimetallic catalysts

with varying Si/Zr ratios (20, 35 and 45). The results confirm that the impregnation of metals is an appropriate method for synthesizing these catalysts. The physicochemical characteristics were done using different analysis methods. The XRD and FT-IR spectra confirm the successful formation of the desired catalysts. On the other hand, in order to determine the amount of metals present in the synthesized structures, XRF test was performed; the results of which show appropriate metal introducing. The results obtained from the characterization tests showed that the catalyst surface properties are the most effective factors in the catalytic performance. In conclusion, the conversion, selectivity, and stability results indicate that the best catalytic behavior was observed for NiZr(35)-ZH catalyst at 150 °C, with high benzene conversion (82%), the highest benzene selectivity (78%), and low coke formation (0.9 wt%). The results prove the dependence of the hydrogenation reaction to active phase dispersion ( $M_d$ ) and the catalytic acidity in the hydrogenation reaction of benzene. Furthermore, kinetic tests carried out under various conditions confirm that bimetallic catalysts supported on micro-mesoporous molecular sieves have a significant effect on reaction rate and activation energy, making them an attractive choice for selective benzene hydrogenation.

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