n-pentane isomerization over Pt-Al promoted sulfated zirconia nanocatalyst

M. Ejtemaei[a,b], N. Charchi Aghdam[a,b], A.A. Babaluo[a,b,*], A. Tavakoli[a,b] and B. Bayati[a,b,c]

a. *Department of Chemical Engineering, Sahand University of Technology, Tabriz, P.O. Box 51335/1996, Iran.*
b. *Nanostructure Materials Research Center (NMRC), Sahand University of Technology, Tabriz, P.O. Box 51335/1996, Iran.*
c. *Department of Chemical Engineering, Ilam University, Ilam, Iran.*

Abstract. Platinum containing sulfated zirconia (Pt-SZ/Al) catalyst was prepared by precipitation method. Characterization of the prepared catalyst was performed using XRD and SEM, and catalytic activity was studied for isomerization of nC_5 at atmospheric conditions and temperatures of 180-240°C in a flow reactor. The effects of reaction temperature, H_2/nC_5 ratio, and WHSV were investigated. As revealed by SEM and XRD, the prepared sulfated zirconia was of nanoscale size and had predominantly tetragonal crystalline phase. n-pentane conversion increased with increasing temperature and selectivity decreased. The optimal reaction temperature was 220°C where n-pentane conversion and isopentane selectivity were 70% and 94%, respectively. The positive effect of H_2/nC_5 ratio was observed on nC_5 conversion and iC_5 selectivity in the investigated H_2/nC_5 ratio range. This trend of variation was related to the role of acid and metallic sites on the reaction pathway. As expected, increase in the WHSV, which reduces contact time between reactant and catalyst, decreased nC_5 conversion and increased selectivity toward iC_5. The RON of the product increased with increasing temperature; then, it showed slight decrease at higher temperature. The decrease in the activation energy was observed, which can be attributed to the different reaction mechanisms or different rate-determining steps.

1. Introduction

In recent years, owing to environmental regulations on gasoline composition, much attention has been paid to supply of clean gasoline with high RON, low content of olefins and aromatics such as benzene, and low concentration of sulfur [1-4]. In this sense, isomerization of light paraffin using solid acid catalysts, as a key technology in the production of clean fuels, has been raised [2-5]. These reactions are limited by thermo-dynamic equilibrium, favoring low temperatures [6,7]. Many recent efforts are focused on improving and development of this process.

Solid acids such as H-mordenite, H-MFI-based catalysts, Friedal-Craft catalysts such as $AlCl_3$, heteropoly acids, etc. have been widely studied in alkane isomerization [4,5,8-10]. Studies on the employed catalysts for this reaction showed that Sulfated Zirconia (SZ), as an environmentally friendly catalyst, was believed to be the most promising catalyst among the solid acids due to low-temperature hydrocarbon skeletal rearrangements for thermodynamic consideration [6,7,10-12].

Sulfated zirconia as a solid super acid was first

*. *Corresponding author. Tel.: +98 413 3459081;*
   Fax: +98 413 3444355
   E-mail address: a.babaluo@sut.ac.ir (A.A. Babaluo)

reported by Holm and Baily in 1962 for the isomerization of hydrocarbons. The activity and selectivity of zirconia catalysts are significantly influenced by preparation method, zirconia crystalline phase, and various other parameters [13]. Sulfated zirconia exists in three crystallographic structures: monoclinic, tetragonal, and cubic, of which only cubic and tetragonal phases of SZ are catalytically active [14].

Studies on the n-alkane isomerization show that isomerization of C_4-C_6 paraffin can be effectively catalyzed by environmentally friendly sulfated zirconia catalysts [4,6,13,15-18]. Catalytic performances of sulfated zirconia catalysts in n-pentane isomerization, as the main components of the hydrocarbons composing light naphtha, obtained by a number of groups, are listed in Table 1. As can be seen, only a few papers have been devoted to n-pentane isomerization at atmospheric conditions. In 2000, Risch and Wolf [15] studied n-pentane isomerization over SZ and Pt promoted SZ catalysts at atmospheric conditions. Their studies showed that activity of sulfated zirconia catalysts depended on the pretreatment procedure and degree of hydration. Later on, in 2004, Vijay and Wolf [13] reported n-pentane isomerization over Pt promoted SZ catalyst at atmospheric conditions. They showed that proper calcination and pretreatment affected the activity of the catalyst. Notably, although sulfated zirconia catalysts had been successfully used for n-pentane isomerization, their catalytic activity and/or selectivity were still relatively low, especially at atmospheric conditions.

Although the industrial processes are operated under high pressure of hydrogen [9], it is desirable to carry out isomerization at low pressure from the viewpoint of safety. In addition, low pressure presents advantages such as facility and low operating costs. In this work, the Pt promoted SZ catalyst was prepared by precipitation method [21]. Isomerization of n-pentane to iso-pentane was further investigated over the prepared catalyst under atmospheric conditions. An assessment of reaction variables, including the reaction temperature, hydrogen-to-hydrocarbon molar ratio, and spatial velocity, in the feed for the n-pentane isomerization was performed. The octane properties of the isomerizate, yields of branched isomers, and reaction pathway under different reaction conditions were also studied.

2. Experimental

2.1. Catalyst preparation
The bifunctional catalyst used in this work consists of SZAl as acid function and Pt as metallic component, which was prepared as described in the literature [21]. Briefly, zirconium hydroxide was prepared by precipitation of aqueous solution of $ZrOCl_2.8H_2O$ (BDH Laboratory Supplies Poole) with 26% ammonia solution (Aldrich) at pH 10. The precipitate was filtered and washed with deionized water until the disappearance of chloride ions (AgNO$_3$ test) after ageing at 338 K for 24 h. The obtained $Zr(OH)_4$ sample was mixed with the required amount of bohemite (based on 15 wt.% Al). Thereafter, it was sulfated using 0.5 M of sulfuric acid solution. The solid was filtered and dried for 12 h at 110°C. Pt was introduced by an incipient wetness technique with an aqueous solution of hexachloroplatinic acid (Merck). The platinum content was 0.5 wt.%. Then, the sample was dried at 110°C for 12 h. Finally, the synthesized powder was calcined at 500°C for 3 h.

2.2. Catalyst characterization
The XRD pattern of the sulfated zirconia sample for phase identification and crystallite size determination was measured with a Philips X-ray diffractometer, Model Bruker D8 Advance, using Cu Kα radiation in the range of $2\theta = 20 - 70°$. The morphology of the sample was analyzed using SEM image recorded by the model HITACHI S-4160 and Quanta tax-QX2 scanning electron microscope.

2.3. Reaction procedures
The hydroisomerization process for n-pentane was run in a flow-type fixed-bed reactor loaded with 1.0 g of prepared catalyst (20/40 mesh) at the temperature ranging between 180-240°C under atmospheric pressure. The experimental set-up is shown in Figure 1. Before the catalytic reaction experiment, the catalyst was pretreated in situ with flowing air at 450°C for 3 h in order to remove the water adsorbed on the surface. Then, the temperature was lowered to 250°C and the catalyst was reduced in flowing hydrogen for 3 h. Afterwards, hydrogen and nC_5 mixture was introduced into the reactor. The gas phase was continuously sampled and analyzed in an on-line Teif Gostar gas

Table 1. Results of the isomerization of nC_5 over different SZ based catalysts.

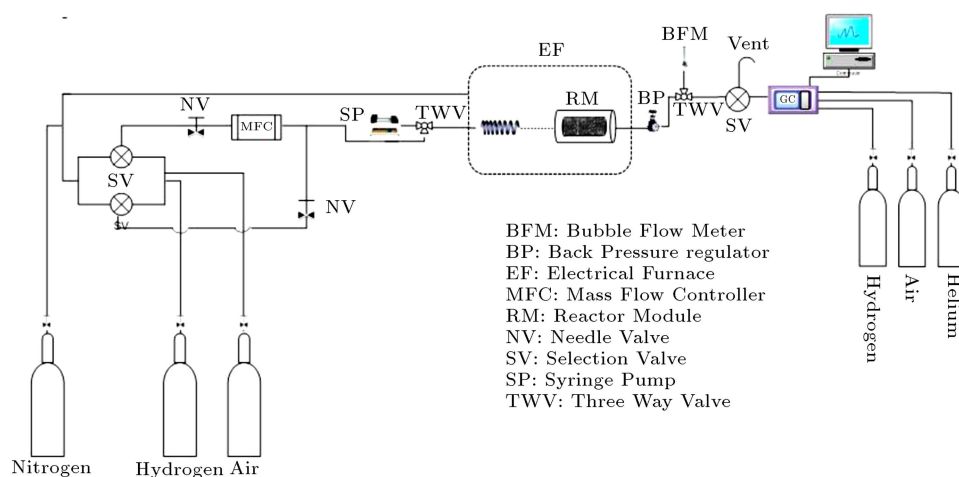| Catalyst	X (%)	S_{iso} (%)	P (atm)	T (°C)	Ref.
Pt/SZ	10	95	1	250	[15]
Pt/SZ	19	92	1	250	[15]
Cu/SZ	53.14	98	34	150	[17]
Pt/SiO$_2$+SZ	78	62	34	200	[12]
Pt/SZ	76	62	1	250	[13]
Pt-Pd/SZ	73*	—	31	200	[8]
Pt/SZ	77.6	13	—	30	[19]
	51.5	19.5			
Pt/SZ	52.47	20.42	2.07	100	[20]

*: Yield.

Figure 1. Experimental set-up for isomerization of n-pentane under atmospheric pressure.

chromatograph equipped with a capillary column and an FID (Cat. No. TR-110222, Serial No: p2085307, TRB-1, Tecknokroma, l:25 m, ID:0.25) detector to analyze the reaction products.

The catalytic performance was evaluated through n-pentane conversion, isopentane selectivity, and yield of isomerization by using the following equations:

$$X_{n-\text{pentane}} = \frac{\sum A_i - A_{n-\text{pentane}}}{\sum A_i} \times 100, \qquad (1)$$

$$S_i = \frac{A_i}{\sum A_i - A_{n-\text{pentane}}} \times 100, \qquad (2)$$

$$Y_i = \frac{X_{n-\text{pentane}} \times S_i}{100}, \qquad (3)$$

where A_i is the corrected chromatographic area for a particular compound.

3. Results and discussion

3.1. Characterization

The XRD pattern of the synthesized catalyst is shown in Figure 2. As can be seen, tetragonal zirconia phase with the crystallite size of 13.9 nm is formed with $2\theta = 30.2°$, $34.5°$, $50.2°$, and $60.2°$ for the (1 0 1), (0 0 2), (1 1 2), and (2 1 1) reflections [14]. Crystallite size of tetragonal phase was determined from the characteristic peaks ($2\theta = 30.2$) using Scherrer formula with a shape factor (K) of $0.94 : D = (0.94\lambda/\beta\cos\theta$, where D is the crystallite size (nm), λ is the radiation wavelength (0.1540598 nm), θ is the diffraction peak angle, and β is the corrected half-width at half-maximum intensity (FWHM) [14].

SEM image of the synthesized powder is presented in Figure 3. Obviously, nanopowders with sizes of about 30-40 nm have been synthesized.

3.2. Isomerization activity

3.2.1. Effect of reaction temperature

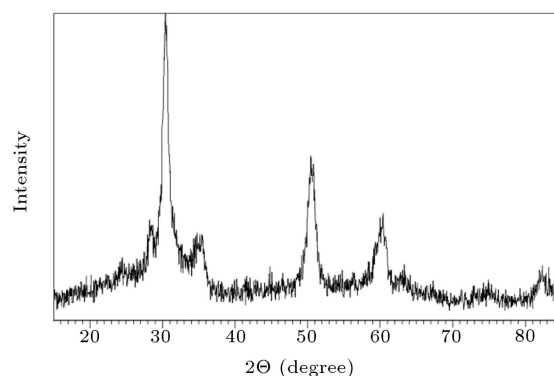Figure 4 shows the conversion and the product selec-
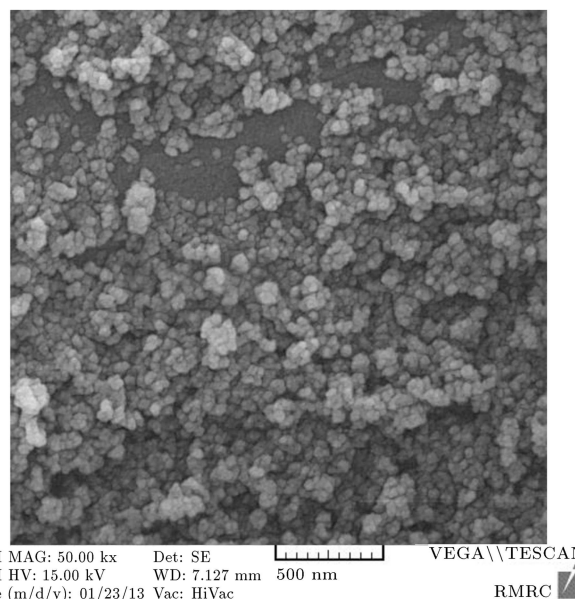

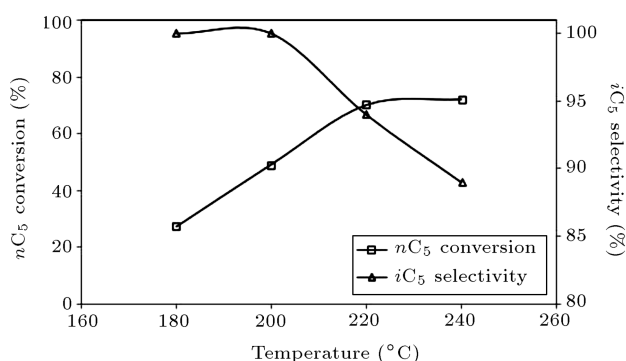**Figure 2.** XRD pattern of the SZ sample.

Figure 3. SEM image of the SZ sample.

Figure 4. The dependence of n-pentane conversion and iso-pentane selectivity on reaction temperature. P: atmospheric pressure; mol H_2/mol $nC_5 = 9.6$; WHSV = 8.8 (mmol of feed gas/g.h).

Figure 6. The effect of reaction temperature on iC_5 yield. P: atmospheric pressure; mol H_2/mol $nC_5 = 9.6$; WHSV = 8.8 (mmol of feed gas/g.h).

tivity data obtained in the isomerization of n-pentane as a function of reaction temperature over the prepared catalyst. The reaction was operated at the temperature ranging from 180 to 240°C, atmospheric pressure, and H_2/nC_5 of 9.6. It can be seen that the nC_5 conversion increases linearly with increasing reaction temperature for low temperatures and increases more gradually at higher temperatures.

The selectivity to isopentane is equal to 100% at 180-200°C; increasing the temperature beyond 200°C lowers the selectivity and it reaches 89% at 240°C. This is due to occurrence of side reactions at higher temperatures.

The thermodynamic equilibrium distribution is a function of temperature with low temperature favoring high thermodynamic concentrations of branched isomers. The equilibrium iso-C_5 ratio (isopentanes content in sum of pentanes) [22] and experimental data on the prepared catalyst are represented in Figure 5. It is evident from the results that isopentane/n-pentane ratio increases with temperature and after reaching a maximum, it decreases. As can be seen, the isopentane/n-pentane ratio attained at lower tempera-
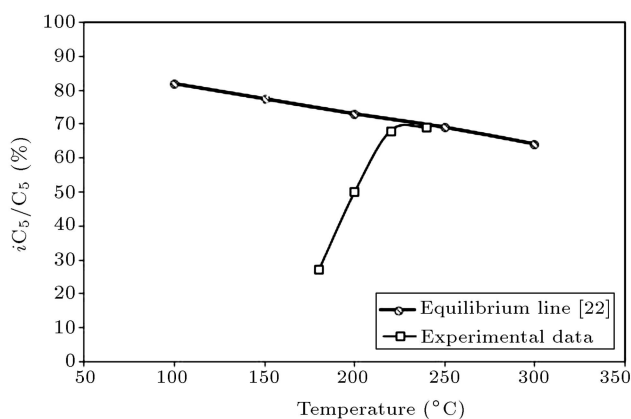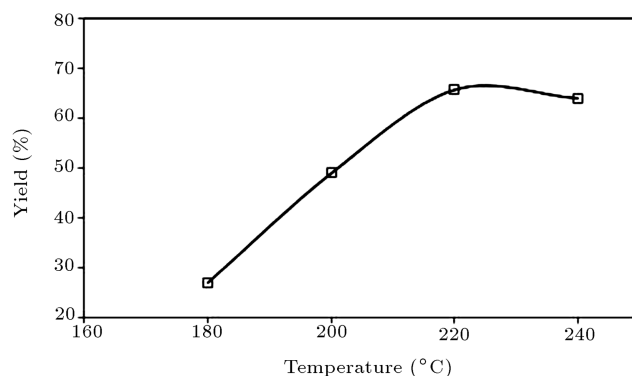
tures is far below the equilibrium ratio; around 220°C, it approaches equilibrium and at higher temperatures, thermodynamic equilibrium between n-pentanes and isopentane is practically established. This behavior is a consequence of the kinetic limitation at low temperature and thermodynamic limitation at higher temperatures. Thus, based on these findings, the fact that the conversion showed gradual increase at higher temperatures is attributed to thermodynamic limitation [22].

In order to obtain optimum value of the reaction temperature, the variation of the isopentane yield with temperature is presented in Figure 6. It is found that 220°C is the proper reaction temperature at which maximum yield of isopentane can be achieved.

3.2.2. Effect of H_2/nC_5 molar ratio

The effect of H_2/n-pentane feed ratio on catalytic properties is presented in Figure 7. When hydrogen to n-pentane ratio changes, conversion rate and reaction selectivity are affected in a different way. Selectivity to isopentane improved as the hydrogen to n-pentane ratio increased from 1 to 12, while conversion increased first and reached about 66% and 73% for temperatures of 220°C and 240°C, respectively; however, it did not
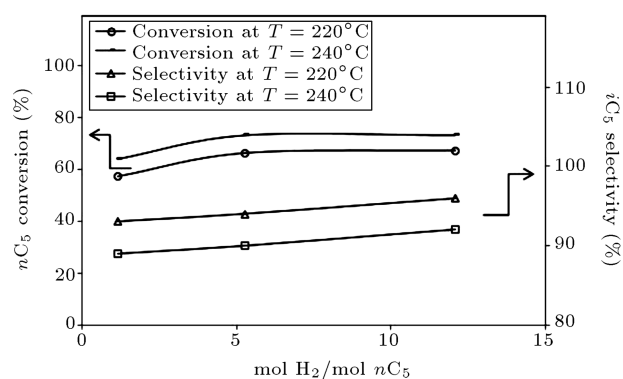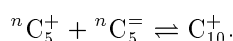

Figure 5. The variation of iso-C_5 ratio with temperature. P: atmospheric pressure; mol H_2/mol nC_5=9.6; WHSV=8.8 (mmol of feed gas/g.h).
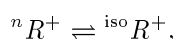

Figure 7. Conversion of n-pentane and selectivity of isopentane as a function of H_2/nC_5 molar ratio. WHSV=11.2 (mmol of feed gas/g.h).

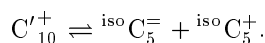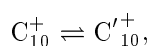further increase at higher hydrogen to n-pentane ratios (between 5 and 12).

It is well known that the isomerization reaction pathway consists of three steps: formation of carbenium ions, followed by rearrangement, and, finally, protonation of newly formed carbenium ions [9]. Although many studies have been reported concerning the way of formation of carbenium ions, the role of metallic site, and the role of hydrogen, there is still controversy regarding many of the details. According to classical bifunctional mechanism, the alkane is dehydrogenated to an alkene on metallic site. The alkene is then isomerized to a branched alkene on the acid site. The resulting branched alkene is hydrogenated into the branched alkane on the metallic site [9,10,23]. Thus, the positive effect of hydrogen partial pressure on n-pentane isomerization cannot be explained in terms of classical bifunctional mechanism.

It is also proposed that Pt can activate and dissociate hydrogen into hydride and proton species, followed by spillover to the support. Hydride ions lead to an acceleration in the desorption of carbenium ion intermediates; consequently, n-pentane conversion increases [23,24]. It is noteworthy that carbenium ion intermediates can easily undergo dimerization-cracking reaction to form byproducts or polymerize to give coke precursors [9,12]. In other words, rearrangement of carbenium ions can proceed via two possible mechanisms: bimolecular mechanism, which results in relatively low isoalkane selectivity, and monomolecular mechanism, where the selectivity in isopentane is high [3,9,12,25], as shown below:

Monomolecular pathway:

$$^nR^+ \rightleftharpoons {}^{iso}R^+,$$

$$^nC_5^+ + {}^nC_5^= \rightleftharpoons C_{10}^+.$$

Bimolecular pathway:

$$C_{10}^+ \rightleftharpoons C'^{+}_{10},$$

$$C'^{+}_{10} \rightleftharpoons {}^{iso}C_5^= + {}^{iso}C_5^+.$$

Therefore, it is expected that hydrid transfer to carbocation followed by its desorption would relatively suppress the bimolecular pathway involving the reaction of C_5 cations (carbenium ions) with C_5 alkenes and rearrangement step would occur via monomolecular mechanism, leading to high selectivity.

3.2.3. Effect of WHSV

Figure 8 shows effect of space velocity (WHSV) on n-pentane isomerization. As shown in this figure, regardless of whether the reaction temperature is 220°C or 240°C, nC_5 conversion decreases with increasing space
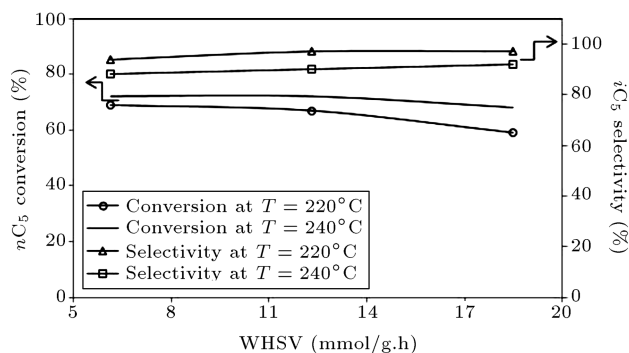

Figure 8. Effect of WHSV on n-pentane conversion and i-pentane selectivity. P: atmospheric pressure; mol H$_2$/mol nC_5=6.

velocity, whereas the isopentane selectivity increases for both reaction temperatures. An increase in space velocity leads to reduction in contact time between reactant and catalyst and, consequently, pentane conversion decreases. Increase in the selectivity of isopentane at higher WHSV is due to the suppression of secondary transformation of isopentane and side reactions.

3.2.4. Research octane number

It is well known that branched alkanes have high Research Octane Numbers (RONs) compared to the linear alkanes and the isomerization (branching) of alkanes is a key reaction for improving the octane number of gasoline. Figure 9 shows the RONs of the feed and product as a function of temperature. The RON of isomerization product was calculated according to Eq. (4):

$$RON = \sum_{i=1}^{n} C_i \times RON_i, \tag{4}$$

where C_i is fraction of component i present in the isomerization product and RON_i is the RON of component i.
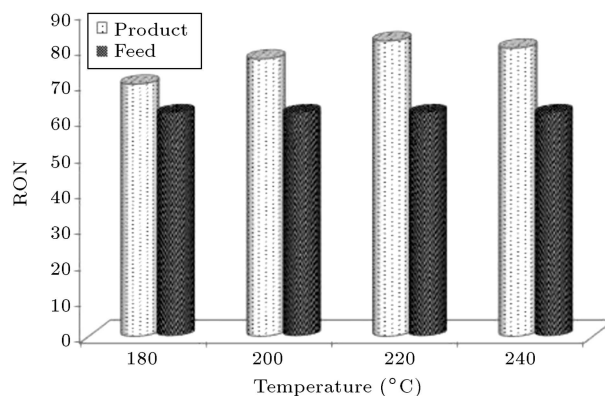

Figure 9. Dependence of RON of the isomerization product on reaction temperature. P: atmospheric pressure; mol H$_2$/mol nC_5 = 9.6; WHSV = 8.8 (mmol of feed gas/g.h).
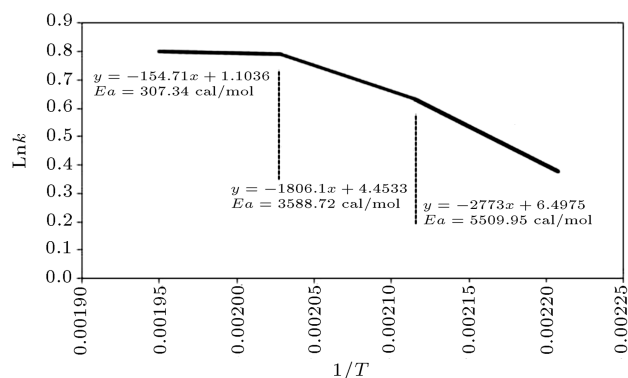
Figure 10. Arrhenius plot for n-pentane isomerization reaction.

As can be seen in Figure 9, the RON of the product increases with increasing temperature; then, it shows slight decrease at higher temperatures. As regards n-pentane isomerization, products consist mainly of isopentane and small amounts of byproducts. Variation of RON with the rise of reaction temperature seems to be closely correlated with the isopentane concentration in the product. Thus, isopentane increases the number of octane products more effectively than others do.

As discussed in Section 1, isopentane concentration increases with increasing temperature and then decreases. Thus, this trend for product RON is expected.

3.2.5. Apparent activation energy

The apparent activation energy has been determined by the Arrhenius plots of the reaction rates in a range of temperatures from 180 to 240°C (Figure 10). As shown in Figure 10, the apparent activation energy values were found with three linear segments.

The apparent activation energy was 5509.95 cal mol^{-1} in the range of 180-200°C, 3588.72 cal mol^{-1} in the range of 200-220°C, and 307.34 cal mol^{-1} in the range of 220-240°C. As can be seen, activation energy values decrease with temperature. Two reasons may be attributed to this behavior; change of the rate-determining step or reaction mechanism [26,27].

Whereas the activation energy of the bimolecular mechanism is lower than that of the monomolecular mechanism [16,25], it is proposed that bimolecular mechanism is predominant at higher temperatures. Also, on the basis of our results in Figure 4, it is found that iC$_5$ selectivity is very high at high temperatures and deceases with increasing temperature. This also confirms the fact that bimolecular mechanism is predominant at higher temperatures.

4. Conclusion

In summary, we investigated the nC$_5$ isomerization on the synthesized Pt/AlSZ catalyst using fixed-bed flow reactor at 180-240°C, as XRD and SEM analyses confirmed the synthesized sulfated zirconia powders are nano-crystalline with mainly tetragonal phase. Catalytic results showed that nC$_5$ conversion increased with the enhancement of reaction temperature and iC$_5$ selectivity decreased. The catalyst exhibited optimum performance in 220°C. The iC$_5$ concentration increased with temperature and then decreased as a consequence of the kinetic limitation at low temperature and thermodynamic limitation at higher temperatures. It was found that increase in H$_2$/nC$_5$ ratio enhanced isomerization reaction. The positive effect of this ratio suggests that the prevailing mechanism is hydrogen-spillover and monomoleculare pathway. It was also observed that the nC$_5$ conversion decreased and iC$_5$ selectivity increased with WHSV due to the decrease in the contact time. The RON of isomerate increased with the increase of treatment up to 220°C, while the further increase of temperature beyond 220°C led to a slight decrease of isomerate octane number. The calculated activation energies were found to decrease with temperature, which probably implies that biomolecular mechanism became predominant.

References

1. Kimura, T. "Development of Pt-SO$_4^{2-}$/ZrO$_2$ catalyst for isomerization of light naphtha", *Catal. Today*, **81**, pp. 57-63 (2003).

2. Song, H., Wang, N., Song, H.L., Li, F. and Jin, Z. "Effect of Al content on the isomerization performance of solid super acid Pd-S$_2$O$_8^{2-}$/ZrO$_2$-Al$_2$O$_3$", *Chin. J. Chem. Eng.*, **22**(11-12), pp. 1226-1231 (2014).

3. Miyaji, A., Echizen, T., Li, L., Suzuki, T., Yoshinaga, Y. and Okuhara, T. "Selectivity and mechanism for skeletal isomerization of alkanes over typical solid acids and their Pt-promoted catalysts", *Catal. Today.*, **74**, pp. 291-297 (2002).

4. Yu, G.X., Lin, D.L., Hu, Y., Zhou, X.L., Li, C.L., Chen, L.F. and Wang, J.A. "RE$_2$O$_3$-promoted Pt-SO$_4^{2-}$/ZrO$_2$-Al$_2$O$_3$ catalyst in n-hexane hydroisomerization", *Catal. Today*, **166**, pp. 84-90 (2011).

5. Matsuda, T., Watanabe, K., Sakagami, H. and Takahashi, N. "Catalytic properties of H$_2$-reduced MoO$_3$ and Pt/zeolites for the isomerization of pentane, hexane, and heptane", *Appl. Catal. A: Gen.*, **242**, pp. 267-274 (2003).

6. Yu, G.X., Zhou, X.L., Liu, F., Li, C.L., Chen, L.F. and Wang, J.A. "Effect of isopropanol aging of Zr(OH)$_4$ on n-hexane isomerization over Pt-SO$_4^{2-}$/Al$_2$O$_3$-ZrO$_2$", *Catal. Today*, **148**, pp. 70-74 (2009).

7. Silva-Rodrigo, R., Cruz-Domínguez, E.L., Lugo-del Angel, F.E., Navarrete-Bolaños, J., García-Alamilla, R., Olivas-Sarabia, A., Melo-Banda, J.A., Cruz-Netro, L.C., Zamora-Ramírez, G. and Castillo-Mares, A. "Studies of sulphated mixed oxides (ZrO$_2$-SO$_4$-La$_2$O$_3$) in the isomerization of n-hexane", *Catal. Today*, **250**, pp. 197-208 (2015).

8. Watanabe, K., Kawakami, T., Baba, K., Oshio, N. and Kimura, T. "Effect of metals on the catalytic activity of sulfated zirconia for light naphtha isomerization", *Catal. Surveys from Asia*, **9**, pp. 17-24 (2005), DOI: 10.1007/s10563-005-3333-0.

9. Ono, Y. "A survey of the mechanism in catalytic isomerization of alkanes", *Catal. Today*, **81**, pp. 3-16 (2003).

10. Liu, Y., Na, K. and Misono, M. "Skeletal isomerization of n-pentane over Pt-promoted cesium hydrogen salts of 12-tungstophosphoric acid", *J. Mol. Catal. A: Chem.*, **141**, pp. 145-153 (1999).

11. Zhou, X.L., Yu, G.X., Tang, C., Li, C.L., Wang, J.A., Novaro, O., Llanos, M.E. and Cortés-Jácome, Ma.A. "On the role of calcination temperature in Pt-SO$_4^{2-}$/ZrO$_2$-Al$_2$O$_3$ preparation and catalytic behaviors during the n-hexane hydroisomerization", *Catal. Lett.*, **124**, pp. 277-283 (2008).

12. Essayem, N., Ben Taârit, Y., Feche, C., Gayraud, P.Y., Sapaly, G. and Naccache, C. "Comparative study of n-pentane isomerization over solid acid catalysts, heteropolyacid, sulfated zirconia, and mordenite: dependence on hydrogen and platinum addition", *J. Catal.*, **219**, pp. 97-106 (2003).

13. Vijay, S. and Wolf, E.E. "A highly active and stable platinum-modified sulfated zirconia catalyst 1. Preparation and activity for n-pentane isomerization", *Appl. Catal. A.*, **264**, pp. 117-124 (2004).

14. Heshmatpour, F. and Babadi Aghakhanpour, R. "Synthesis and characterization of superfine pure tetragonal nanocrystalline sulfated zirconia powder by a non-alkoxide sol-gel route", *Adv. Powder Technol.*, **23**, pp. 80-87 (2012).

15. Risch, M. and Wolf, E.E. "n-Butane and n-pentane isomerization over mesoporous and conventional sulfated zirconia catalysts", *Catal. Today*, **62**, pp. 255-268 (2000).

16. Matsuhashi, H., Shibata, H., Nakamura, H. and Arata, K. "Skeletal isomerization mechanism of alkanes over solid superacid of sulfated zirconia", *Appl. Catal. A: Gen.*, **187**, pp. 99-106 (1999).

17. Pérez-Luna, M., Consultchi, A., Toledo-Antonio, J.A. and Cortés-Jácome, M.A. "n-pentane isomerization over Pt- and Ni-Pt-promoted sulfated zirconia catalysts supported on alumina", *Catal. Lett.*, **131**, pp. 285-293 (2009).

18. Song, H., Wang, N., Song, H.L. and Li, F. "La-Ni modified S$_2$O$_8^{2-}$/ZrO$_2$-Al$_2$O$_3$ catalyst in n-pentane hydroisomerization", *Catal. Commun.*, **59**, pp. 61-64 (2015).

19. Occelli, M.L., Schiraldi, D.A., Auroux, A., Keogh, R.A. and Davis, B.H. "Effects of copper on the activity of sulfated zirconia catalysts for n-pentane isomerization", *Appl. Catal. A: Gen.*, **209**, pp. 165-177 (2001).

20. Zhao, J., Yue, Y., Hua, W., He, H. and Gao, Z. "Catalytic activities and properties of sulfated zirconia supported on mesostructured γ-Al$_2$O$_3$", *Appl. Catal. A: Gen.*, **336**, pp. 133-139 (2008).

21. Yu, G.X., Zhou, X.L., Tang, C., Li, C.L., Wang, J.A. and Novaro, O. "A comparative study of the synthesis approaches and catalytic behaviors of Pt/SO$_4^{2-}$/ZrO$_2$-Al$_2$O$_3$ catalysts for n-hexane hydroisomerization", *Catal. Commun.*, **9**, pp. 1770-1774 (2008).

22. Yasakova, E.A. and Sitdikova, A.V. "Tendency of isomerization process development in Russia and foreign countries", *Oil and Gas Business*, UDC 665.656.2 (http://www.ogbus.ru/eng) (2010).

23. Løften, T. "Catalytic isomerization of light alkanes", Doctoral thesis, Norwegian University of Science and Technology (2004).

24. Zhang, A., Nakamura, I., Aimoto, K. and Fujimoto, K. "Isomerization of n-pentane and other light hydrocarbons on hybrid catalyst. Effect of hydrogen spillover", *Ind. Eng. Chem.*, **34**, pp. 1074-1080 (1995).

25. Wakayama, T. and Matsuhashi, H. "Reaction of linear, branched, and cyclic alkanes catalyzed by Brönsted and Lewis acids on H-mordenite, H-beta, and sulfated zirconia", *J. Mol. Catal. A: Chemical*, **239**, pp. 32-40 (2005).

26. Tomishige, K., Okabe, A. and Fujimoto, K. "Effect of hydrogen on n-butane isomerization over Pt-SO$_4^{2-}$/ZrO$_2$ and Pt/SiO$_2$+SO$_4^{2-}$-ZrO$_2$", *Appl. Catal. A: Gen.*, **194-195**, pp. 383-393 (2000).

27. Demirci, Ü.B. and Garin, F. "Kinetic study of n-heptane conversion on sulfated zirconia-supported platinum catalyst: the metal-proton adduct is the active site", *J. Mol. Catal. A: Chem.*, **188**, pp. 233-243 (2002).

Biographies

Mahboobeh Ejtemaei received her BSc and MSc degrees in Chemical Engineering from Sahand University of Technology, Tabriz, Iran, in 2009 and 2011, respectively. Her research interests include nanocatalyst, reaction, isomerization processes, membrane reactor, and nanocomposite membranes gas separation.

Nazanin Charchi Aghdam received her BSc degree in Chemical Engineering from Amirkabir University of Technology, Tehran, Iran, in 2008, and MSc degree in Chemical Engineering from Sahand University of

Technology in 2011. Her research interests are in the area of membrane reactors, heterogeneous catalysts, reaction, zeolite synthesis and charachterization, zeolite membrane, and separation science, especially gas separation by membrane.

Ali Akbar Babaluo, after graduation from high school in 1992, continued his education in Chemical-Petrochemical Engineering at Sahand University of Technology (SUT). Then, he continued his education and graduated with PhD degree in 2004. Afterwards, Dr. Babaluo continued his education and research-based activities at SUT as Assistant Professor. In the last decade, he has presented different specialized courses in BSc, MSc, and PhD degrees; his research and technical-based activities have strongly been continued, of which some of the most important activities are publishing more than 80 journal papers and more than 150 national and international conference papers; performing research projects, 13 completed and 4 in run; supervising more than 55 MSc and PhD theses; and obtaining 16 national patents (2 patents have scientific certificate). He has been awarded 10 times as selected researcher at different levels.

Dr. Babaluo has also performed other different scientific activities such as: publishing a journal; creating research centers and incubators; writing books and book chapters; working as an editorial board member of two research journals; and presenting scientific comments, corrections, and corrigendum on published articles. Now, he continues his viable activities at Sahand University of Technology as a Full Professor.

Akram Tavakoli was born in 1976. She received BSc, MSc, and PhD degrees in Chemical Engineering from Amirkabir University of Technology, Tehran, Iran. In 2007, she joined Sahand University of Technology, Tabriz, Iran. She is now working in the academic staff at Sahand University. Her interests include thermo-kinetics and nanotechnology fields.

Behrouz Bayati received the BSc degree in Chemical Engineering from Islamic Azad University of Arak, Iran, in 2003, and MSc and PhD degrees in Chemical Engineering from Sahand University of Technology, Iran, in 2007 and 2013, respectively. He is currently an Assistant Professor of Chemical Engineering at Ilam University. His research interests are membrane process, molecular simulation, and modeling of separation processes. He has published over 10 research articles on related subjects. In the last decade, he has presented different specialized courses.