

An impact of Re on Pt-Re/SO₄ – ZrO₂ catalyst for *n*-hexane isomerization

A. R. ZARUBICA^{ab*}, P. PUTANOV^c, D. KOSTIC^b, G. BOSKOVIC^a

^aFaculty of Technology, University of Novi Sad, Cara Lazara 1, 21000 Novi Sad, Serbia

^bFaculty of Science, University of Nis, Visegradska 33, 18000 Nis, Serbia

^cSerbian Academy of Sciences and Arts, Knez Mihajlova 35, 11000 Belgrade, Serbia

The effect of modification of bare sulfated zirconia catalyst by platinum, and rhenium loaded next to platinum in *n*-hexane isomerization has been shown. The promotion of unmodified sulfated zirconia by metallic components increases primary isomerization activity of catalyst. Besides, the impact of rhenium in bimetallic sulfated zirconia based catalyst is revealed. Moreover, it is established that impact of rhenium on platinum dispersion is favorable, but not enough for catalytic efficiency. Activity and/or selectivity of the mentioned mono- and bimetallic catalysts depend on favorable textural features, critical crystallite size, moderate acidity and finally on platinum dispersion.

(Received May 28, 2010; accepted July 14, 2010)

Keywords: Impact of platinum/rhenium, Isomerization of *n*-hexane, Sulfated zirconia

1. Introduction

The recent EU limits on some of environmental unfriendly substances presenting at the same time high octane number (ON) have caused a problem for refineries to provide gasoline characterized by high-quality performances. Therefore, hydroisomerization of middle *n*-hydrocarbons (C₅–C₇) offers a promising way to solve the problem by providing high-ON isomers. Conventional technologies assume an application of either traditional chlorided-alumina-based or zeolite-based catalysts [1]. Former are very active, however undergo easy poisoning by impurities in feed and can cause a problem due to environmental unfriendly promoter, while the latter ones being resistant to poisoning exhibit lower activity, and require higher reaction temperatures. For that reason, solid acids like Fe₂O₃, SnO₂, ZrO₂, TiO₂, etc., have become very popular as catalysts for *n*-alkanes isomerization reactions. Among them, sulfated zirconia (SZ), alone as well as together with metal promoters, is a promising solution based on two points of view, catalytic efficiency and green chemistry requirements. Unfortunately, the bare SZ suffers from a fast deactivation and although regeneration is possible, a short operating cycle makes it impractical. An addition of various metals may be used in order to increase its stability. A design of new environmental friendly metal(s)-SZ (M-SZ) isomerization catalysts is a task [2-4]. The topic of this paper dealing with the modification of SZ-based catalysts by one/two metals in view of the fact that a concept of dual zirconia promotion is not often a subject of scientific debates [5, 6]. The intention is to correlate physicochemical and catalytic performances of Pt-modified SZ and Pt-Re-modified SZ catalysts additionally regarding to roles of rhenium and/or platinum.

2. Experimental part

In order to prepare metal(s)-SZ catalyst samples, zirconia-based supports were synthesized from Zr(IV)-isopropoxide by a modified sol-gel method [7,8], however, by using pH 9.0 proved to result in the advantageous physico-chemical properties [9]. The obtained hydroxide was sulphated for the nominal sulphur loading of 3.0 mass % following calcinations at 600°C for 3h [8]. Platinum was introduced by an impregnation of sulphated zirconia with H₂PtCl₆ solution (Aldrich, Co.) using the incipient wetness technique to get Pt loading of 0.5 mass % (Pt-SZ sample). Rhenium was incorporated by a multi-step addition of alcohol solution of ReCl₅ (Aldrich, Co.) to obtain the second metal loading of 0.5 mass %. By following that procedure next sample was obtained Pt-Re-SZ with platinum initially introduced. Additional catalyst calcinations at 450°C for 3h in synthetic air flow of 25 ml/min followed the incorporation of every particular metal.

Physicochemical properties of catalyst samples were investigated by means of their textural (Low Temperature Nitrogen Adsorption/Desorption, ASAP 2000), structural (XRD, Philips), morphological (SEM, JOEL JSM-6460LV) and surface (FTIR, Nicolet) properties. Dispersion of Pt was checked by O₂/H₂ titration at room temperature. The adsorptions of pyridine on preevacuated catalyst samples, following additional final evacuation in order to remove physisorbed pyridine, preceded FTIR measurements. Catalytic activity was tested in isomerisation of *n*-hexane reaction at 250°C, at atmospheric pressure, using H₂ (He in the case of SZ) premixed with *n*-C₆ (H₂/*n*-C₆ = 15), and space velocity 6·10⁻² mmol *n*-C₆/g_{cat}·min. As a rule 0.5 g of a fresh catalyst sample was loaded into a quartz micro-reactor and *in situ* reduced in hydrogen flow of 20 ml/min at 300 or

350°C for 2.5 h preceding the reaction. The reaction lasted 80–600 min depending on the steady state moment. The reaction products were separated on PONA 50 m long capillary column at 35°C, using 1 ml/min N₂ as carrier gas, and analyzed by gas chromatograph (HP 5890) equipped with a FID detector. Activities of different catalysts samples were ranked by means of *n*-hexane conversion normalized by the number of C-atoms in the products. Product composition comprised hydrocarbons starting with CH₄ to benzene, and selectivity was calculated as a sum of monobranched (2- and 3-methylpentane) and dibranched (2,2- and 2,3-dimethylbutane) C₆-isomers.

3. Results and discussion

Data presented in Table 1 show that Pt introduced to SZ catalyst changes its both textural and structural properties, *i.e.* increases surface area and enhances the fraction of tetragonal zirconia crystal phase known as catalytic active in reaction of *n*-alkane isomerization [10]. The use of both unpromoted and Pt-promoted catalysts for *n*-hexane isomerization has presented almost identical initial activities at the same reaction temperature of 200°C (not shown) [11]. In the case of unpromoted SZ catalyst, however, fast deactivation can be observed as the result of

coke accumulation after the initial conversion of reactant due to the absence of hydrogen, *i.e.* autoregeneration conditions [12]. It has to be mentioned, however, that the use of *n*-C₆ mixed with He probably as the main cause for SZ catalyst deactivation by coke, was a need taking into account that unmodified SZ catalyst showed no activity using H₂ or N₂ as carrier gases [13]. The similar exclusivity of He in terms of SZ catalyst activity was noticed earlier in the case of different reactants, *n*-hexane [3] as well as *n*-heptane [14]. As it was reported earlier [11], the activity profile of Pt-SZ is quite different, and starting from the same initial conversion as in the case of unpromoted catalyst, slowly reaches relatively high steady state conversion [11]. This is in contrast to some claims on the initial inhibiting effect of Pt on SZ, at least in case of *n*-butane and *n*-pentane isomerization [15]. Obviously, platinum in this paper, in the presence of H₂, primarily acts in terms of decreasing of deactivation rate by means of hydrogenation of coke-precursors on the catalyst surface. Therefore, the same initial activities for both unpromoted and Pt promoted catalysts, and slowly rising activity to the steady-state point in the case of latter one speaks in favor of stabilizing/modifying role of platinum, rather than a promoting one [11,16].

Table 1. Textural and structural properties of metal promoted SZ-based catalysts

Sample	Specific surface area (m ² /g)	Mean pore diameter (nm)	X _{200/250} (°C)	Pore volume (cm ³ /g)	Ratio of tetragonal/monoclinic crystal phase of SZ (%)	Crystallite size of SZ tetragonal phase (nm)
SZ	92.5	5.4	10/13*	0.176	88/12	13
Pt-SZ	116.4	4.6	18/60**	0.143	94/6	8
Pt-Re-SZ	101.1	5.4	12/35**	0.144	95/5	8

* reaction temperature 200/300°C

** reaction temperature 200/250°C

Bimetallic platinum-rhenium modified SZ based catalyst shows favorable textural properties characterized by the improved features comparing to the unmodified SZ catalyst (Table 1). This catalyst exhibits almost equal pore volume and similar specific surface area as monometallic Pt-SZ catalyst, decreased in the order Pt-Re/SZ ~ Pt/SZ > SZ. Similar discussion on textural features of mono- and bimetallic reforming catalysts (platinum and platinum-rhenium alumina based catalysts) cited comparable values of specific surface areas after the introduction of the second metal [17]. The contents on platinum and the second metal are quite similar in both cases. The XRD patterns (not shown) of mono- and bimetallic catalysts are quite comparable to that one of a typical SZ. Structural properties reveals that the incorporation of Pt brings stability to the primary SZ-based catalyst by increasing the fraction of catalytical active tetragonal crystal phase and decreasing its crystallite size [3,4,11,18]. It has been commonly accepted that tetragonal crystalline phase of the SZ-based catalytic systems, as well as critical value of particle size are both known as important for catalytic

efficiency in *n*-alkane isomerization reaction [11,19,20]. It seems that Pt plays a crucial role as both textural and structural promoter of SZ by stabilizing the catalytic active tetragonal crystal phase, keeping its crystallite size below critical value of 10 nm [21], and consequently delaying process of sintering. In addition, the introduction of rhenium as the second metal has increased the dispersion of platinum starting with 7 up to 21% on the catalyst surface, as is proved by H₂/O₂ titrations. This may be additional reason why bimetallic platinum-rhenium catalyst presents even higher fraction of tetragonal crystal phase among the investigated catalysts and crystallite size smaller than the critical value for catalyst to be active one (Table 1). Roughly similar situation was established earlier [17], the platinum dispersion was increased by introducing rhenium in bimetallic reforming catalyst supported on γ -alumina. In other words, the grafting of the second metal (rhenium) does not change nano-size character of zirconia crystallites.

Surface properties of catalysts described as their acidic nature are presented in Table 2. They are given in

form of IR-absorbance intensities at wavenumbers characteristic for the adsorbed pyridine, and expressed as concentrations of Brønsted and/or Lewis acid sites (BAS and LAS). BAS are dominant in the case of monometallic Pt-SZ catalyst. Furthermore, the authors suggest the existence of two LAS types (at 1490 and 1610 cm^{-1}) or these may be related to two types of sulfate groups differing in a decomposition rate [22,23]. Both, BAS and LAS, are predominant in the firstly mentioned monometallic catalyst (Pt-SZ). These data may speak on its acidity as promising feature related to relevant activity (Tables 1,2) [4,11,24]. Some authors have earlier claimed Lewis acidity as key role for the activity and selectivity of metallic promoted sulfated based catalysts in *n*-hexane isomerization [25].

Table 2. Absorbance intensities related to BAS and LAS.

Sample	A_{LAS} (at 1490 cm^{-1})	A_{BAS} (at 1540 cm^{-1})	A_{LAS} (at 1610 cm^{-1})
Pt-SZ	0.046	0.027	0.009
Pt-Re-SZ	0.017	0.013	0.004

SEM images representing morphological properties of catalysts prove similarities in crystallite sizes previously estimated by the XRD results (Table 1 and Fig. 1). Smaller particles are recorded in the Pt-SZ catalyst, and particle sizes in catalyst where rhenium is loaded next to platinum, Pt-Re-SZ, are completely comparable confirming again the same findings as revealed by the XRD measurements.

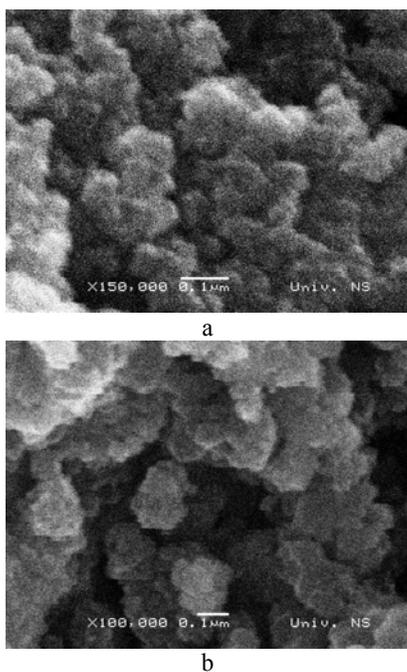


Fig. 1. SEM images of mono- and doubly promoted SZ-based catalysts: a - Pt-SZ; b - Pt-Re-SZ (at different but comparable magnification)

All discussed properties have an impact on catalyst activities in *n*-hexane isomerization reaction (not shown). Pt-loaded SZ-catalyst performs an initial activity at as low as 175°C and reaches significant isomer yield at 200°C. The same promoter has a multifunctional role, being both the acidity improver and stabilizer of the SZ-catalyst. In the case of bimetallic catalyst (Pt-Re-SZ), better catalytic performances were obtained after reduction at higher temperature, *i.e.* 350°C. The increase of reduction temperature for 50°C (up to 350°C) brings some differences to catalytic performances (catalytic activity and reaction yield) of bimetallic catalyst sample. Finally, it is important to underline that the increased reduction temperature applied on the Pt-Re-SZ catalyst, brings it characteristics almost a half of those achieved for Pt-SZ catalyst under the same conditions.

It is commonly accepted that Pt-Re-oxide support catalyst is bifunctional one wherein noble metal acts as center for chemisorption and activation of reactants and the oxide support additionally helps spill-over mechanism in hydrogenation/dehydrogenation of alkenes/alkanes [26,27]. It is already shown in our discussion that the introduction of rhenium next to platinum increased the platinum dispersion similar to findings of other authors [28]. These have explained higher activity of Pt-Re/TiO₂ comparing to Pt/TiO₂ catalyst due to a favorable change of metal dispersion [28], but reactions were different in the two studies. However, in contrast, in our case, Pt-Re-SZ catalyst showed lower activity than Pt-SZ catalyst probably due to few reasons: (i) at least a part of rhenium is present in the oxidized form ReO_x (revealed by the XRD analysis) especially at here applied reduction temperatures, (ii) ReO_x may took part in redox route of reaction mechanism diminishing the isomers yield, (iii) the increase of platinum dispersion is the affirmative reason for improvement of catalytic activity but not sufficient one. Beside that, we suggest that sulfated zirconia also performs different influence on final catalytic performances in contrast to titania. Additional reason is difference in reaction types, and consequently in reaction mechanisms in case of water gas shift reaction [26] based on the use of Pt-Re/TiO₂ comparing to Pt-Re/SZ in isomerization of *n*-hexane in our study. It has to be also stated that these reactions comprise different reactions routes.

4. Conclusions

The obtained data indicate that modification of bare SZ catalyst by Pt significantly increases its isomerization activity, and also converts reaction mechanism to bifunctional one. In addition dual modification by Pt and Re improves also catalytic activity to a certain extent. This is caused by the improvement of textural characteristics (specific surface area and pore volume), stabilized structural characteristics (crystallite size below critical value), and higher, but moderate acidity, these together are favorable to rearrangement of reactant molecules (*n*-hexane) and isomerization beginning.

The conversion of *n*-hexane increases in the following order: SZ < Pt-Re/SZ < Pt/SZ. Among them, mono- and bimetallic promoted SZ catalysts undergo to bifunctional reaction route, while unmodified sulfated zirconia takes part in the oxidative dehydrogenation reaction during isomerization expressing only the initial activity. Platinum loaded SZ-catalyst performs such activity at as low temperature as 175°C and reaches significant C₆-isomers yield at 200°C.

Pt-Re-SZ catalyst performs features almost a half of those demonstrated by the Pt-SZ catalyst under the same process conditions. As a consequence of additional loading of rhenium next to platinum, the increase of platinum dispersion performs as desirable feature in view of improvement of catalytic activity but not enough one.

Acknowledgements

Financial supports of Serbian Ministry of Science and Technological Development (Project: “To Green Chemistry via Catalysis”, ON 142024) and Serbian Academy of Sciences and Arts are highly appreciated.

References

- [1] H. Weyda, E. Kohler, *Catal. Today* **81**, 51 (2003).
- [2] T. Buchholz, U. Wild, M. Muhler, G. Resofszki, Z. Paal, *Appl. Catal. A: General* **189**, 225 (1999).
- [3] K. Föttinger, G. Kinger, H. Vinek, *Appl. Catal. A: General* **266**, 195 (2004).
- [4] E.A. Blekkan, K.A. Johnsen, T. Loften, *React. Kinet. Catal. Lett.* **86**, 149 (2005).
- [5] E.A. García, E.H. Rueda, A.J. Rouco, *Appl. Catal. A: General* **210**, 363 (2001).
- [6] S.-T. Wong, T. Li, S. Cheng, J.-F. Lee, C.-Y. Mou, *Appl. Catal. A: General* **296**, 90 (2005).
- [7] C. Breitung, A. Garsuch, H. Papp, *Appl. Catal. A: General* **296**, 148 (2005).
- [8] A.R. Zarubica, M.N. Miljkovic, E.E. Kiss, G. C. Boskovic, *React. Kinet. Catal. Lett.* **90**, 145 (2007).
- [9] G. Boskovic, A. Zarubica, P. Putanov, *J. Optoelectr. Adv. Mater.* **9**, 2251 (2007).
- [10] J. M. Parera, *Catal. Today* **15**, 481 (1992).
- [11] A.R. Zarubica, G. Boskovic, P. Putanov, D. Kostic, M. Pohl, *J. Optoelectr. Adv. Mater.* **12**, 1183 (2010).
- [12] G. Boskovic, M. Baerns, “Catalyst Deactivation” in M. Baerns (Ed.): *Basic Principles of Applied Catalysis*, Springer-Verlag, Berlin, Heidelberg 2004, p. 479.
- [13] A. Zarubica, P. Putanov, G. Boskovic, *J. Serb. Chem. Soc.* **72**, 679 (2007).
- [14] K. Föttinger, E. Halwax, H. Vinek, *Appl. Catal. A: General* **301**, 115 (2006).
- [15] M. Risch, E. E. Wolf, *Stud. Surf. Sci. Catal.*, **13th ICC** **1**, 2381 (2000).
- [16] S. Vijay, E. E. Wolf, *Appl. Catal. A: General* **264**, 117 (2004).
- [17] I. Coletto, R. Roldan, C. Jimenez-Sanchidrian, J.P. Gomez, F. J. Romero-Salguero, *Fuel* **86**, 1000 (2007).
- [18] A. Zarubica, G. Boskovic, *Euroanalysis XIV, Book of Abstracts*, Antwerp, Belgium, 2007, p. 893.
- [19] C. Morterra, G. Cerrato, F. Pinna, M. Signoretto, *J. Catal.*, **157**, 109 (1995).
- [20] J. M. Parera, *Catal. Today*, **15**, 481 (1992).
- [21] R. C. Garvie, M. F. Goss, *J. Mater. Sci.*, **21**, 1253 (1986).
- [22] G.C. Boskovic, A.R. Zarubica, M.N. Kovacevic, P.S. Putanov, *J. Therm. Anal. Cal.* **91**, 849 (2008).
- [23] A. Zarubica, B. Jovic, A. Nikolic, P. Putanov, G. Boskovic, *J. Serb. Chem. Soc.* **74**, 1429 (2009).
- [24] A. Zarubica, G. Bošković, P. Putanov, *Europacat VIII*, Turku, Finland, 2007, P9-66 (CD-Rom).
- [25] G. Volkova, S. Reshetnikov, L. Shkuratova, A. Budneva, E. Paukshtis, *Chem. Eng J.* **134**, 106 (2007).
- [26] K.G. Azzam, I.V. Babich, K. Sechan, L. Lefferts, *Appl. Catal. B: Environ.* **80**, 129 (2008).
- [27] G. Olympiou, C. Kalamaras, C. Zeinalipour-Yazdi, A. Efstathiou, *Catal. Today* **127**, 304 (2007).
- [28] H. Iida, A. Igrashi, *Appl. Catal. A: Gen.* **303**, 192 (2006).

*Corresponding author: zarubica2000@yahoo.com