



DOI: 10.22144/ctu.jen.2017.043

Determination of coke on promoted zirconium oxide catalysts in the isomerization reaction of pentane and hexane mixture at high pressure

Nguyen Dien Trung¹, Luu Cam Loc² and Nguyen Tri²¹Department of Chemistry, School of Education, Can Tho University, Vietnam,²Institute of Chemical Technology, Vietnam Academy of Science and Technology, Vietnam

Article info.

Received 28 Oct 2016

Revised 23 Dec 2016

Accepted 31 Oct 2017

Keywords

Hexane, isomerization, pentane, Pt/ZrAl, Pt/ZrS, Pt/ZrW

ABSTRACT

A series of bifunctional catalysts, including sulfated zirconia, tungstated zirconia and alumina-supported zirconia as effective supports for Pt was prepared for isomerization reaction of pentane and hexane mixture at 7 atm. The structure and the surface property of denatured zirconium oxide catalysts were characterized by using physico-chemical methods such as X-ray diffraction, Brunauer–Emmett–Teller, scanning electron microscopy, transmission electron microscopy and temperature programmed reduction. Catalytic activity and stability in the isomerization reaction were studied in a micro-flow reactor under pressure of 7 atm and at 250 °C, and molar ratio of H₂: hydrocarbon mixture of 5.92. The coke deposited on catalyst surface was determined by a burn-off method. The mass of coke on Pt/ZrO₂-γ-Al₂O₃ (Pt/ZrAl), Pt/ZrO₂-SO₄ (Pt/ZrS) and Pt/ZrO₂-WO₃ (Pt/ZrW) was 5.23%, 4.06% and 1.23% respectively.

Cited as: Trung, N.D., Loc, L.C. and Tri, N., 2017. Determination of coke on promoted zirconium oxide catalysts in the isomerization reaction of pentane and hexane mixture at high pressure. Can Tho University Journal of Science. 7: 13-18.

1 INTRODUCTION

The isomerization of pentane and hexane mixture is an essential process to produce iso-paraffins for low aromatics gasoline. The isomerization reaction is commonly catalyzed by bifunctional catalysts consisting of noble metals (Pd, Pt) supported on micro-porous, acidic supports (zeolite, acidic oxide). These bifunctional catalysts have been widely used for the isomerization reaction. In the paraffin isomerization, pressure does not affect thermodynamic equilibrium. However, increasing the pressure on isomerization reaction involving hydrogenation limits coke formation in catalysts.

Among available supports, zirconium oxide (ZrO₂) plays an important role in heterogeneous catalyst because ZrO₂ is both a support and a catalyst. ZrO₂ used as a support in many reactions due to its high

thermal stability and oxygen storage ability. However, ZrO₂ generally has the low surface area and ununiformed structure by burning (Souza *et al.*, 2001). Thus, activity of ZrO₂ catalyst rapidly dropped due to the loss of surface species. More effective techniques to hybridize stable active species on the catalyst surface have been developed. A number of composite catalysts including ZrO₂-γ-Al₂O₃, ZrO₂-SO₄ and ZrO₂-WO₃ have been developed to enhance surface area and the catalyst activity.

One of the major problems related to the operation of heterogeneous catalysis is the loss of catalytic activity, called deactivation. Deactivation can be caused by many different factors such as poisoning, phase transformation and coking. The coke formation on the surface of catalysts is an essential factor that lead to deactivate the catalyst either by

covering of the active sites and by blocking pores (Forzatti and Lietti, 1999). Burn-off method is an easy way to determine the mass of coke on catalyst surface in laboratory.

2 EXPERIMENTS

2.1 Synthesis of catalysts

2.1.1 Materials

For the preparation of catalysts, zirconyl chloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, Merck, 99.0%), phosphotungstic acid hydrate ($\text{H}_3[\text{P}(\text{W}_3\text{O}_{10})_4] \cdot \text{H}_2\text{O}$, Merck, 97.0%), aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Guanghua, 99.0%), ammonium solution (NH_3 , Guanghua, 25.0–28.0%), sulfuric acid solution (H_2SO_4 , Guanghua, 95.0–98.0%) and deionized water were used.

2.1.2 Synthesis of Pt/ZrAl catalyst

At first, $\text{Al}(\text{OH})_3$ gel was prepared by aluminum nitrate solution 13% and then dropwise ammonia solution 5% up to a pH of 8 to 9. $\text{Al}(\text{OH})_3$ gel was aged for 24 h. $\text{Al}(\text{OH})_3$ precipitate was filtered, washed with distilled water and ethanol to eliminate NO_3^- ions. The obtained gel was dried naturally for 12 h to form $\text{Al}(\text{OH})_3$. The following stage, $\text{Zr}(\text{OH})_4$ gel was prepared from a solution containing 13% ZrOCl_2 . Ammonia solution 5% was added dropwise under constant stirring until a pH value of 10. Gel aging process occurred for 24 h. The obtained precipitate of $\text{Zr}(\text{OH})_4$ was filtered and washed with distilled water to eliminate Cl^- ions. $\text{Zr}(\text{OH})_4$ gel was naturally dried by air for 12 h. The next stage, $\text{Al}(\text{OH})_3$ gel and $\text{Zr}(\text{OH})_4$ gel were mixed together for 1 h to form an identical mixture. Obtained mixture was aged overnight, dried at 110°C for 6 h and then calcined at 600°C in an air stream for 3 h. This support was identified as ZrO_2 - γ - Al_2O_3 (ZrAl). After calcination, the sample was impregnated by 1.93×10^{-3} M H_2PtCl_6 solution of a concentration to obtain a catalyst containing 0.5 wt% Pt. Finally, the catalyst was dried at 110°C for 3 h and then calcined at 500°C in an air stream for 3 h. This catalyst was called Pt/ZrAl (Mariana *et al.*, 2005).

2.1.3 Synthesis of Pt/ZrS catalyst

At first, $\text{Zr}(\text{OH})_4$ gel was dried at 110°C for 6 h. Sulfate was added by soaking of $\text{Zr}(\text{OH})_4$ gel in 0.5 M H_2SO_4 solution and stirred for 1 h to obtain a catalyst containing 35 wt% sulfate. The following stage, sample was dried at 110°C for 6 h and ZrO_2 -

SO_4 (ZrS) support catalyst obtained by calcining dried sample at 700°C in air stream for 3 h. Finally, 1.93×10^{-3} M H_2PtCl_6 solution was added to produce a material containing 0.7 wt% Pt. The material was dried at 110°C for 3 h and then calcined at 500°C in an air stream for 3 h. This denatured zirconium oxide catalyst was recognized as Pt/ZrS (Triwahyono *et al.*, 2006.).

2.1.4 Synthesis of Pt/ZrW catalyst

$\text{Zr}(\text{OH})_4$ after dried in a stove at 110°C for 6 h was soaked with $\text{H}_3\text{P}(\text{W}_3\text{O}_{10})_4$ solid to obtain a support containing 15 wt% tungsten. The sample was placed in a stove at 110°C for 6 h and finally calcined at 800°C in an air stream for 3 h. This support was termed ZrO_2 - WO_3 (ZrW). After calcination, the support was impregnated by 1.93×10^{-3} M H_2PtCl_6 solution to produce a material containing 0.5 wt% Pt. The material was dried at 110°C for 3 h and then calcined at 500°C in an air stream for 3 h. This bifunctional catalyst was identified as Pt/ZrW (Comelli *et al.*, 1998).

2.2 Physico-chemical investigation of catalysts

X-ray diffraction (XRD) measurements were performed on Bruker D8 Advance X-Ray Diffractometer with Cu K_α radiation (1.54 Å) at 50 kV and 250 mA. The spectra were recorded in the 2θ from 2° to 70° range. Specific surface area was determined by N_2 -adsorption-desorption isotherm at 77 K with Nova Quantachrome. To show the morphology of catalysts, scanning electron microscope (SEM) was performed with JEOL JEM 7401. In addition, in order to determine the crystal shape and homogeneity of the catalysts, transmission electron microscopy was carried out in JEOL JEM 1400. Finally, Altamira Ami 200 was used to determine degrees of reduction of Pt^{2+} cations in the prepared catalysts.

2.3 Activity investigation of catalysts

Catalytic activity in hexane and pentane isomerization was tested by a micro-flow reactor under pressure of 7 atm at temperature range of 200 – 450°C ; pentane and hexane concentration in feed of 4.6 mol%; molar ratio of H_2 : hydrocarbon mixture of 5.92; feed flow of 5 L/h, and catalyst weight of 1.0 g. The reaction mixture was analyzed on the GC Agilent Technologies 6890 Plus with a FID detector, and DB 624 column with 30 m of length and 0.32 mm of outer diameter.

Table 1: Conditions in the isomerization reaction of pentane and hexane mixture

Parameters	Value
Mass of catalyst (g)	1.00
Pressure (atm)	7
Temperature survey (°C)	200–450
Flow rate (L/h)	5
Materials	Pentane and hexane mixture with mole ratio of 1 : 1
Temperature of oven reaction (°C)	27
RON	43.3

Before carrying out the reaction, catalysts were reduced by hydrogen at 500°C for 2 h. Hydrogens flow rate was 2 L/min. Stability of catalysts was carried out at optimized temperature survey until conversion of catalysts decreased 30%.

2.4 Determination of coke

Mass and formula of coke on the catalysts were determined by water and carbon dioxide from burning of coke. Catalysts were treated by nitrogen flow for 15 minutes, followed by heated up to 500°C and kept at this temperature for 2 h. Ascarite was used as a chemical to adsorb carbon dioxide and water absorbent was anhydron. Determination of coke formation on catalysts ended when mass of anhydron and ascarite was a constant.

Mass of carbon/catalyst (g/g):

$$m_c = m_{CO_2} \times \frac{12}{44} \times \frac{1}{m_{catalyst}} \quad (1)$$

Mass of hydrogen/catalyst (g/g):

$$m_H = m_{H_2O} \times \frac{2}{18} \times \frac{1}{m_{catalyst}} \quad (2)$$

Mass of coke/catalyst (g/g): $m_{coke} = m_c + m_H$ (3)

Fomula of coke $(C_x H_y)_n$:

$$x : y = \frac{m_c}{12} : \frac{m_H}{1} \quad (4)$$

3 RESULTS AND DISCUSSION

3.1 The physico-chemical properties of catalysts

It can be seen from Figure 1a that XRD pattern of Pt/ZrW sample contains the peaks at about 2θ: 30.2°, 50.2°, 50.7° and 60.1°, which were assigned to tetragonal phase of ZrO₂ while the peaks at about 2θ: 28.2°, 31.4°, 34.3°, 35.2° and 55.5° were assigned to monoclinic phase of ZrO₂. Moreover, the peaks of monoclinic WO₃ were observed at 2θ: 23.1°, 23.6° and 24.6°. Pt was absent on XRD spectrum of Pt/ZrW. For Pt/ZrS sample (Figure 1b), the peaks at 2θ = 24.5°, 28.2°, 31.4°, 34.3°, 35.2°, 49.4°, 50.4°, 54.3°, 55.5° and 59.9° were assigned to monoclinic phase of ZrO₂. The peaks of Pt at 2θ = 39.8, 46.2 and 67.5° with weak intensity were also observed. The characteristic peaks of γ-Al₂O₃ and Pt were absent on XRD spectrum of Pt/ZrAl (Figure 1c). For Pt/ZrAl, the peaks located at 2θ: 30.2, 35.1, 50.4 and 60.5° were characterized the tetragonal phase of ZrO₂.

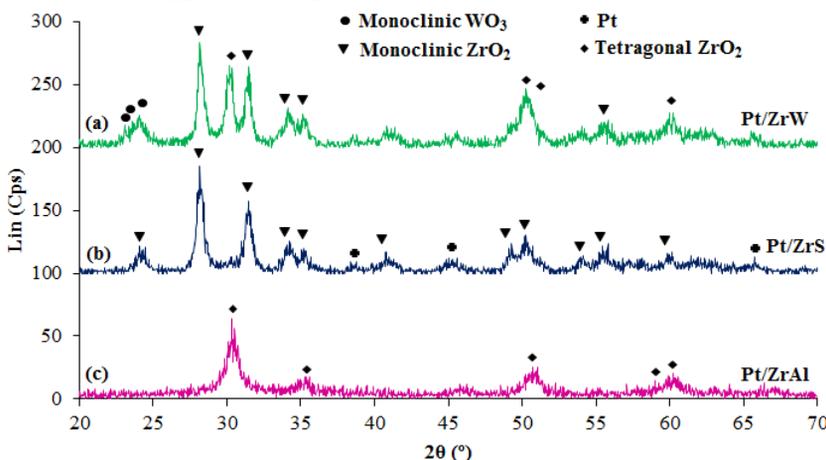


Fig. 1: XRD spectrum of catalysts: Pt/ZrW (a), Pt/ZrS (b) and Pt/ZrAl (c)

Results of XRD spectrum showed that the γ - Al_2O_3 existed in amorphous phase and ZrO_2 in tetragonal or monoclinic phase (Smolikov *et al.*, 2010). The generation of WO_3 on Pt/ZrW catalyst implying that at high calcination temperature ZrO_2 - WO_3 may be cut in order to expel WO_3 on the surface (Barrera *et al.*, 2005; Canavese *et al.*, 2010). In addition, no XRD signal corresponding to Pt was detected on prepared catalysts (Pt/ZrAl and Pt/ZrW) due to the low of 0.5% Pt concentration and good dispersal on supports ZrAl and ZrW. However, Pt were observed on Pt/ZrS due to concentration of Pt is high (Barrera *et al.*, 2005; Canavese *et al.*, 2010).

It has been shown in Table 2 that the specific surface area of Pt/ZrAl catalyst was lower than that of γ - Al_2O_3 (250–350 m^2/g), but much higher than that

of ZrO_2 (8–25 m^2/g) (Yori *et al.*, 2000; Monica and Stefano, 2005). Moreover, denaturing ZrO_2 with H_2SO_4 and $\text{H}_3[\text{P}(\text{W}_3\text{O}_{10})]$ also enhanced the surface area of catalysts significantly.

Table 2: Surface area (S_{BET}), dimension of catalyst particle by scanning electron microscopy (d_{SEM}) and Pt clusters by transmission electron microscopy (d_{TEM}), and reduction degree (K_{Red}) of Pt of catalysts

Catalysts	S_{BET} (m^2/g)	d_{SEM} (nm)	d_{TEM} (nm)	K_{Red} (%)
Pt/ZrW	29.0	35–40	1.80	1.9
Pt/ZrS	57.0	20–25	1.79–1.99	5.3
Pt/ZrAl	201.2	30–43	1.84–1.86	32.9

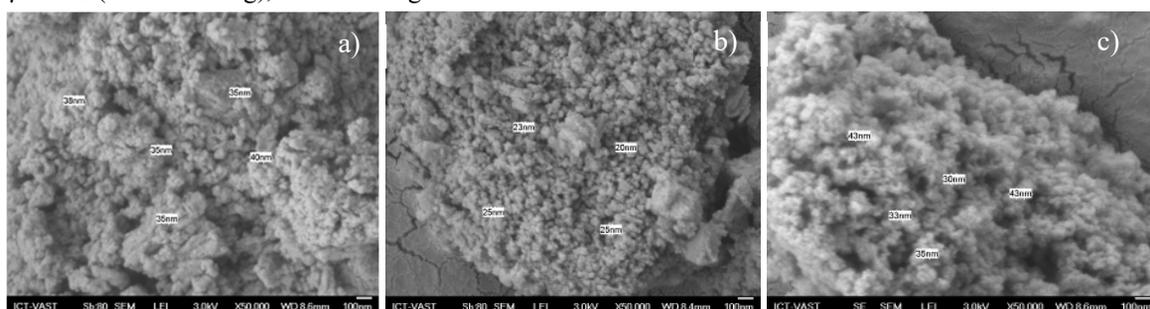


Fig. 2: SEM images of catalysts: Pt/ZrW (a), Pt/ZrS (b) and Pt/ZrAl (c)

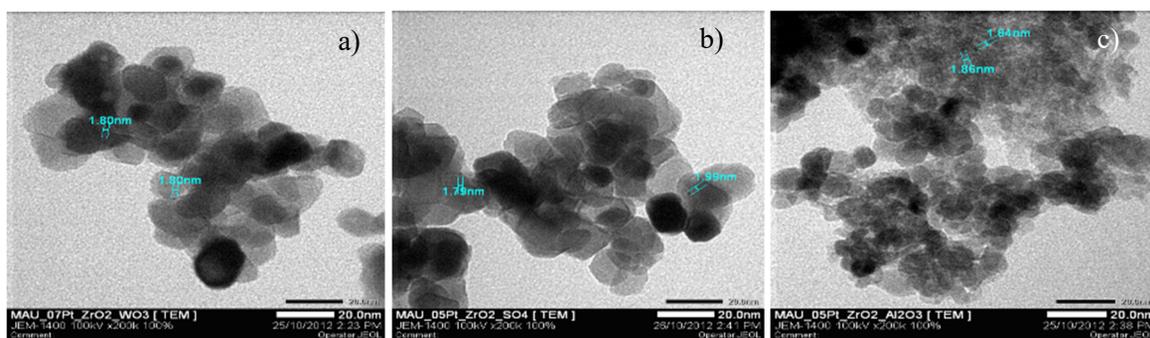


Fig. 3: TEM images of catalysts: Pt/ZrW (a), Pt/ZrS (b) and Pt/ZrAl (c)

From the results presented in Figure 2 and Figure 3 and Table 2, it can be noted that supports were porous materials and formed different clusters. Size of support clusters was from 20 to 43 nm. On supports ZrW, ZrS and ZrAl, the Pt dispersed on supports with dimension of about 2 nm. Results of SEM and TEM showed that Pt well-dispersed on catalysts: Pt/ZrW, Pt/ZrS and Pt/ZrW.

As indicated in Figure 4, on catalysts: Pt/ZrW, Pt/ZrS and Pt/ZrAl, reduction peaks about 200°C can be related to reduction of Pt^{2+} ions (Souza *et*

al., 2001; Grau *et al.*, 2004; Pedrosa *et al.*, 2008). On Pt/ZrW catalyst (Figure 4a), other peaks at 350°C, 690°C and 820°C assigned to the reduction of WO_x species (Barton *et al.*, 1998). For Pt/ZrS catalyst (Figure 4b), the peak at 560°C is characterized the reduction of surface SO_4^{2-} groups while H_2 spillover on ZrAl support displayed a peak around 420°C on Pt/ZrAl catalyst (Figure 4c) (Comelli *et al.*, 1996; Souza *et al.*, 2001; Grau *et al.*, 2004). Reduction degree of Pt^{2+} ions on ZrAl support was the highest following on ZrS and ZrW.

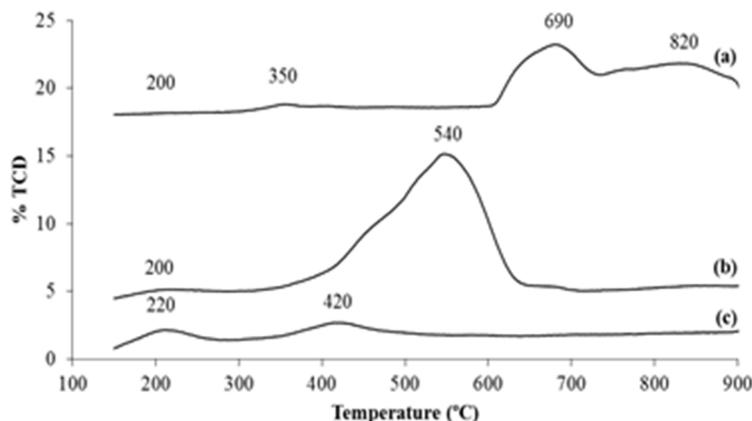


Fig. 4: Temperature programmed reduction profiles of catalysts: Pt/ZrW (a), Pt/ZrS (b) and Pt/ZrAl (c)

3.2 Activity and stability of catalysts

Lifetime of catalysts Pt/ZrW, Pt/ZrS and Pt/ZrAl was also over 30 h when pressure of reaction was 7 atm. High pressure was an important factor to remove coke precursors. On Pt/ZrS, although productivity was high (45%); temperature (525°C) was unfavorable for isomerization reaction. The disadvantage of Pt/ZrAl catalyst is low productivity (19%). However, temperature (375°C) was favorable for isomerization reaction. Pt/ZrW was a favorable catalyst for the conversion of unbranched paraffins to iso-paraffins. After reaction, the research octane number (RON) value of products was increased nearly two times more (43.3 compared with 72.5).

Table 3: Activity and stability of catalysts: Pt/ZrW, Pt/ZrS and Pt/ZrAl

Catalysts	T _{opt} (°C)	X (%)	Y (%)	RON	τ (h)
Pt/ZrW	350	71	60	72.5	> 37.0
Pt/ZrS	525	54	45	62.5	> 30.0
Pt/ZrAl	375	42	19	60.1	> 30.5

3.3 Determination of coke formation

The amount of formed coke is the lowest on Pt/ZrW (1.23%), while this amount is 4.06% and 5.23% on Pt/ZrS and Pt/ZrAl respectively. Carbon content made up 80% of coke on Pt/ZrW and approximately 99% on Pt/ZrS and Pt/ZrAl.

Table 4: Mass and formula of coke formed on the catalysts

Catalysts	m _{coke} /m _{catalyst} (%)	Formula of coke
Pt/ZrW	1.23	(CH ₃) _n
Pt/ZrS	4.06	(C ₁₁ H) _n
Pt/ZrAl	5.23	(C ₁₇ H) _n

Thus, from obtained results W and S showed to be the effective promoters for Pt/Zr catalyst. Catalyst Pt/ZrW promoted by W was the best catalyst for isomerization.

4 CONCLUSIONS

Promotion of Pt-zirconium oxide catalysts by γ -Al₂O₃, SO₄²⁻ and WO₃ led to enhance the surface area of catalysts, dispersion of Pt helped to increase the activity and lifetime of catalysts. The presence of hydrogen limited to the coke formation, therefore, the activity of catalysts was unchanged over 30 h at 7 atm. Pt/ZrW catalyst manifested greater activity and stability, lower coke-formation than other promoted Pt-zirconium oxide catalysts.

REFERENCES

Barrera, A., Montoya, J.A., Viniestra, M., *et al.*, 2005. Isomerization of n-hexane over mono- and bimetallic Pd-Pt catalysts supported on ZrO₂-Al₂O₃-WO_x prepared by sol-gel. *Applied Catalysis A: General*. 290(1): 97-109.

Barton, D.G., Soled, S.L., and Iglesia, E., 1998. Solid acid catalysts based on supported tungsten oxides. *Topics in Catalysis*. 6(1): 87-99.

Canavese, S., Finelli, Z., Busto, M., Benitez, V.B., Vera, C.B., and Yori, J.C., 2010. Poisoning and regeneration of Pt-Pd/WO₃-ZrO₂ short paraffin isomerization catalysts. *Química Nova*. 33: 508-513.

Comelli, R.A., Canavese, S.A., Vaudagna, S.R., and Figoli N.S., 1996. Pt/SO₄-ZrO₂: characterization and influence of pretreatments on n-hexane isomerization. *Applied Catalysis A: General*. 135: 287-299.

Comelli, R.A., Canavese, S.A., and Figoli, N.S., 1998. Effect of operational conditions during n-hexane isomerization over platinum on tungsten-oxide-promoted zirconia. *Catalysis Letters*. 55(3-4): 177-182.

Forzatti, P. and Lietti L., 1999. Catalyst deactivation. *Catalysis Today*. 52(2-3): 165-181.

- Grau, J.M., Yori J.C., Vera, C.R., Lovey, F.C., Condó, A.M., and Parera, J.M., 2004. Crystal phase dependent metal-support interactions in Pt/SO₄-ZrO₂ catalysts for hydroconversion of n-alkanes. *Applied Catalysis A: General*. 265: 141-152.
- Mariana, M.V.M.S. and Martin, S., 2005. Autothermal reforming of methane over Pt/ZrO₂/Al₂O₃ catalysts. *Applied Catalysis A: General*. 281(1-2): 19-24.
- Monica T. and Stefano P.T., 2005. γ -Alumina as a Support for Catalysts: A Review of Fundamental Aspects. *European Journal of Inorganic Chemistry*. 2005(17): 3393-3403.
- Pedrosa, A.M.G., Souza, M.J.B., Marinkovic B.A., Melo, D.M.A., and Araujo, A.S., 2008. Structure and properties of bifunctional catalysts based on zirconia modified by tungsten oxide obtained by polymeric precursor method. *Applied Catalysis A: General*. 342(1-2): 56-62.
- Souza, M.M.V.M., Aranda, D.A.G., Pérez, C.A.C., and Schmal, M., 2001. Reforming of methane with carbon dioxide over Pt/ZrO₂/Al₂O₃ catalysts. *Journal of Catalysis*. 204(2): 498-511.
- Souza, M.M.V.M., Aranda, D.A.G., and Schmal, M., 2001. Surface characterization of zirconia-coated alumina as support for Pt particles. *Physica Status Solidi (a)*. 187(1): 297-303.
- Triwahyono, S., Jalil, A.A., and Halimatun, H., 2006. Isomerization of cyclohexane to methylcyclopentane over Pt/SO₄-ZrO₂ catalyst. *The Institution of Engineers*. 67: 30-35.
- Yori, J.C., Pieck, C.L., and Parera, J.M., 2000. Alkane isomerization on MoO₃/ZrO₂ catalysts. *Catalysis Letters*. 64(2-4): 141-146.