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

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### 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 H<sub>2</sub> : hydrocarbon mixture of 5.92. The coke deposited on catalyst surface was determined by a burn-off method. The mass of coke on Pt/ZrO<sub>2</sub>-γ-Al<sub>2</sub>O<sub>3</sub> (Pt/ZrAl), Pt/ZrO<sub>2</sub>-SO<sub>4</sub> (Pt/ZrS) and Pt/ZrO<sub>2</sub>-WO<sub>3</sub> (Pt/ZrW) was 5.23%, 4.06% and 1.23% respectively.

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### 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 (ZrO<sub>2</sub>) plays an important role in heterogeneous catalyst because ZrO<sub>2</sub> is both a support and a catalyst. ZrO<sub>2</sub> used as a support in many reactions due to its high

thermal stability and oxygen storage ability. However, ZrO<sub>2</sub> generally has the low surface area and ununiformed structure by burning (Souza *et al.*, 2001). Thus, activity of ZrO<sub>2</sub> 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 ZrO<sub>2</sub>-γ-Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>-SO<sub>4</sub> and ZrO<sub>2</sub>-WO<sub>3</sub> 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 ( $\text{NH}_3$ , Guanghua, 25.0–28.0%), sulfuric acid solution ( $\text{H}_2\text{SO}_4$ , Guanghua, 95.0–98.0%) and deionized water were used.

#### 2.1.2 Synthesis of $\text{Pt/ZrAl}$ catalyst

At first,  $\text{Al(OH)}_3$  gel was prepared by aluminum nitrate solution 13% and then dropwised ammonia solution 5% up to a pH of 8 to 9.  $\text{Al(OH)}_3$  gel was aged for 24 h.  $\text{Al(OH)}_3$  precipitate was filtered, washed with distilled water and ethanol to eliminate  $\text{NO}_3^-$  ions. The obtained gel was dried naturally for 12 h to form  $\text{Al(OH)}_3$ . The following stage,  $\text{Zr(OH)}_4$  gel was prepared from a solution containing 13%  $\text{ZrOCl}_2$ . 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  $\text{Zr(OH)}_4$  was filtered and washed with distilled water to eliminate  $\text{Cl}^-$  ions.  $\text{Zr(OH)}_4$  gel was naturally dried by air for 12 h. The next stage,  $\text{Al(OH)}_3$  gel and  $\text{Zr(OH)}_4$  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  $\text{ZrO}_2\text{-}\gamma\text{-Al}_2\text{O}_3$  ( $\text{ZrAl}$ ). After calcination, the sample was impregnated by  $1.93 \times 10^{-3}$  M  $\text{H}_2\text{PtCl}_6$  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  $\text{Pt/ZrAl}$  (Mariana *et al.*, 2005).

#### 2.1.3 Synthesis of $\text{Pt/ZrS}$ catalyst

At first,  $\text{Zr(OH)}_4$  gel was dried at 110°C for 6 h. Sulfate was added by soaking of  $\text{Zr(OH)}_4$  gel in 0.5 M  $\text{H}_2\text{SO}_4$  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  $\text{ZrO}_2\text{-}$

$\text{SO}_4$  ( $\text{ZrS}$ ) support catalyst obtained by calcining dried sample at 700°C in air stream for 3 h. Finally,  $1.93 \times 10^{-3}$  M  $\text{H}_2\text{PtCl}_6$  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  $\text{Pt/ZrS}$  (Tri wahyono *et al.*, 2006.).

#### 2.1.4 Synthesis of $\text{Pt/ZrW}$ catalyst

$\text{Zr(OH)}_4$  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  $\text{ZrO}_2\text{-WO}_3$  ( $\text{ZrW}$ ). After calcination, the support was impregnated by  $1.93 \times 10^{-3}$  M  $\text{H}_2\text{PtCl}_6$  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  $\text{Pt/ZrW}$  (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  $\text{K}_\alpha$  radiation (1.54 Å) at 50 kV and 250 mA. The spectra were recorded in the  $2\theta$  from 2° to 70° range. Specific surface area was determined by  $\text{N}_2$ -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  $\text{Pt}^{2+}$  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  $\text{H}_2$ : 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. Hydrogen 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 anhydrene. Determination of coke formation on catalysts ended when mass of anhydrene 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)

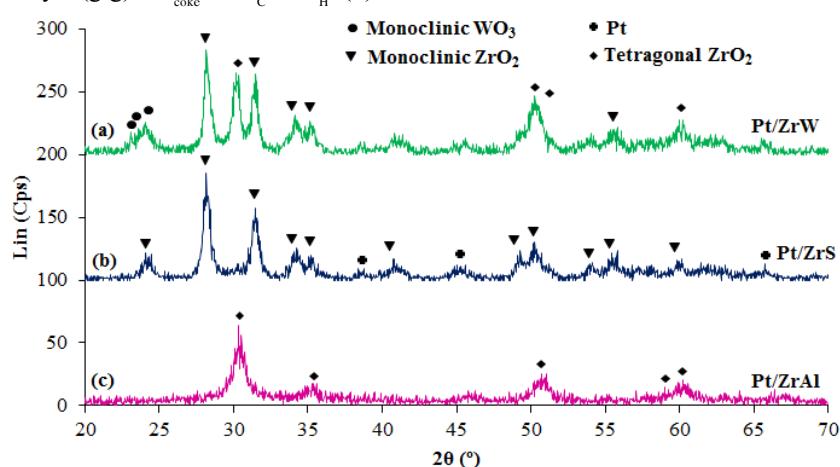
Formula of coke ( $C_x H_y$ )<sub>n</sub>:

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

## 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 20: 30.2°, 50.2°, 50.7° and 60.1°, which were assigned to tetragonal phase of  $ZrO_2$  while the peaks at about 20: 28.2°, 31.4°, 34.3°, 35.2° and 55.5° were assigned to monoclinic phase of  $ZrO_2$ . Moreover, the peaks of monoclinic  $WO_3$  were observed at 20: 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 20 = 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  $ZrO_2$ . The peaks of Pt at 20 = 39.8, 46.2 and 67.5° with weak intense were also observed. The characteristic peaks of  $\gamma-Al_2O_3$  and Pt were absent on XRD spectrum of Pt/ZrAl (Figure 1c). For Pt/ZrAl, the peaks located at 20: 30.2, 35.1, 50.4 and 60.5° were characterized the tetragonal phase of  $ZrO_2$ .



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

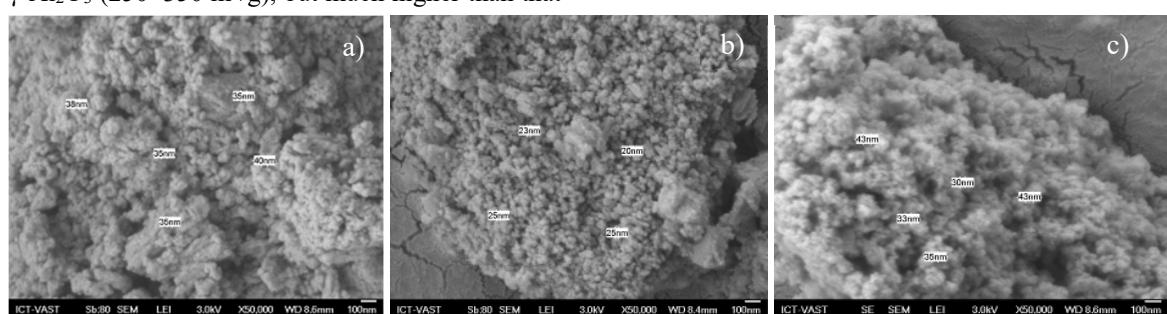
Results of XRD spectrum showed that the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> existed in amorphous phase and ZrO<sub>2</sub> in tetragonal or monoclinic phase (Smolikov *et al.*, 2010). The generation of WO<sub>3</sub> on Pt/ZrW catalyst implying that at high calcination temperature ZrO<sub>2</sub>-WO<sub>3</sub> may be cut in order to expel WO<sub>3</sub> 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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (250–350 m<sup>2</sup>/g), but much higher than that

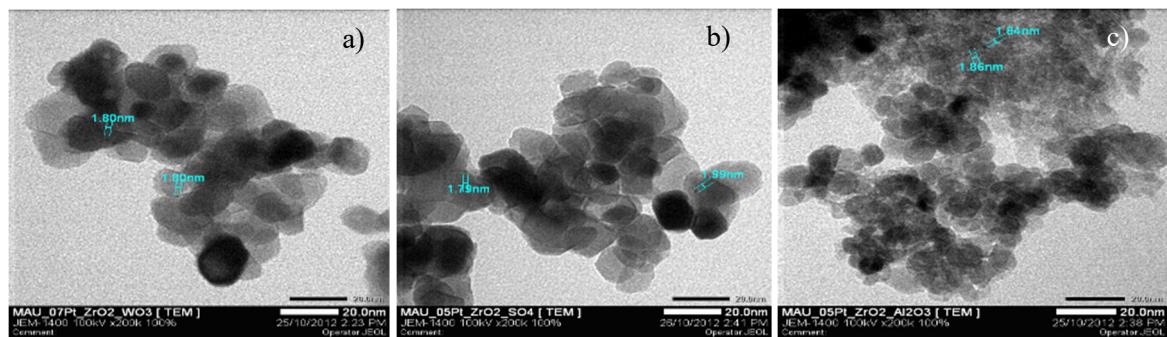
of ZrO<sub>2</sub> (8–25 m<sup>2</sup>/g) (Yori *et al.*, 2000; Monica and Stefano, 2005). Moreover, denaturing ZrO<sub>2</sub> with H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>[P(W<sub>3</sub>O<sub>10</sub>)] also enhanced the surface area of catalysts significantly.

**Table 2: Surface area (SBET), dimension of catalyst particle by scanning electron microscopy (dSEM) and Pt clusters by transmission electron microscopy (dTEM), and reduction degree (K<sub>Red</sub>) of Pt of catalysts**

Catalysts	SBET (m <sup>2</sup> /g)	d <sub>SEM</sub> (nm)	d <sub>TEM</sub> (nm)	K <sub>Red</sub> (%)
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)**

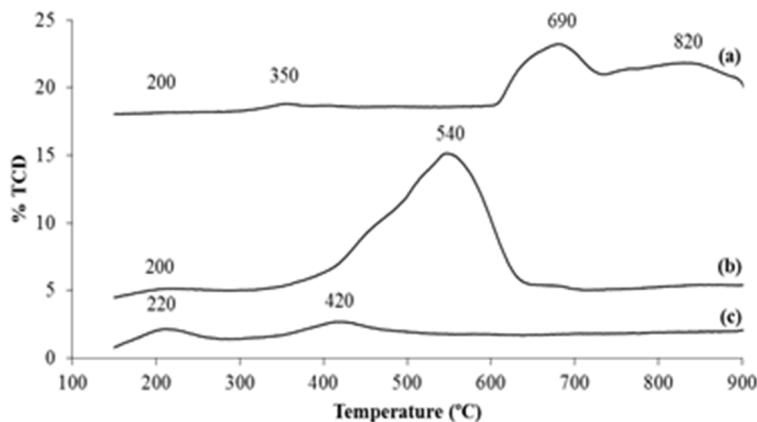


**Fig. 3: TEM images of catalysts: Pt/ZrW (a), Pt/ZrS (b) and Pt/ZrAl (c)**

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<sup>2+</sup> 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<sub>x</sub> species (Barton *et al.*, 1998). For Pt/ZrS catalyst (Figure 4b), the peak at 560°C is characterized the reduction of surface SO<sub>4</sub><sup>2-</sup> groups while H<sub>2</sub> 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<sup>2+</sup> 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 <sub>opt</sub> (°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 <sub>coke</sub> /m <sub>catalyst</sub> (%)	Formula of coke
Pt/ZrW	1.23	(CH <sub>3</sub> ) <sub>n</sub>
Pt/ZrS	4.06	(C <sub>11</sub> H) <sub>n</sub>
Pt/ZrAl	5.23	(C <sub>17</sub> H) <sub>n</sub>

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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SO<sub>4</sub><sup>2-</sup> and WO<sub>3</sub> 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.

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