Catalysis Today 164 (2011) 148–153

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

# Optimizing preparative conditions for tungstated zirconia modified with platinum as catalyst for heptane isomerization

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ARTICLE INFO

*Article history:*
Available online 16 November 2010

*Keywords:*
Tungstated zirconia with platinum
Preparative variables
Heptane isomerization

ABSTRACT

$Pt/WO_3–ZrO_2$ catalysts were prepared under different conditions to optimize the preparative variables for active and selective catalyst in heptane isomerization. The variables examined were (1) pre-drying temperature of hydrous $ZrO_2$, (2) way of impregnation, (3) pH of impregnating solution of ammonium metatungstate, (4) $WO_3$ loading, (5) calcination temperature, (6) calcination atmosphere, and (7) Pt source. In addition to well-known strong effects of (4) and (5), all the variables affected to some extent the activity and selectivity for heptane isomerization. In particular, type of Pt source exerted substantial influence on the activity of the resulting catalyst, $H_4PtCl_6$ performing better than $Pt(NH_3)_4Cl_2$.

## 1. Introduction

Skeletal isomerization of alkanes is a key reaction for production of a gasoline of high quality that contains less aromatics and alkenes but keeps high octane number. Since the alkanes composed of more than 6 carbon atoms easily crack, no catalysts have been developed relevant to an industrial process for hydroisomerization of naphtha containing the fractions heavier than hexane. Since Iglesia's group reported that $Pt/WO_3–ZrO_2$ exhibited high selectivity in heptane isomerization [1,2], a number of studies of isomerization of alkanes have been reported over $Pt/WO_3–ZrO_2$ [3–10]. The catalysts used, however, were prepared by different methods in some points.

The catalytic behaviors of $WO_3–ZrO_2$ and $Pt/WO_3–ZrO_2$ vary depending on the preparative method. It is well known that the calcination temperature and $WO_3$ loading influence much on the catalytic activities. Arata and Hino [11], who synthesized $WO_3–ZrO_2$ for the first time, reported that calcination temperature should be 1073–1123 K, while other researchers calcined $WO_3ZrO_2$ in the temperature range 873–1123 K. The optimum $WO_3$ loading has been reported by a number of researchers to be in the range monolayer to double layer coverage.

In addition to the calcination temperature and $WO_3$ loading, other preparative variables should affect the catalytic properties. Nevertheless, the extent of importance of the variables has not been studied comprehensively. In this study, we examined the effectiveness of the following preparative variables on the activity and selectivity in heptane isomerization. The variables were (1) pre-drying temperature of hydrous $ZrO_2$, (2) way of impregnation, incipient wetness vs. wet impregnation, (3) pH of impregnating solution of ammonium metatungstate, (4) $WO_3$ loading, (5) calcination temperature, (6) calcination atmosphere, and (7) Pt source. A variable of Pt loading was kept constant at 0.5 wt% according to the results of the preceding paper [12]. In addition to well-known strong effects of (4) and (5), all the variables affected to some extent the activity and selectivity for heptane isomerization. In particular, type of Pt source exerted substantial influence on the activity of the resulting catalyst, $H_4PtCl_6$ performing better than $Pt(NH_3)_4Cl_2$.

## 2. Material and methods

$WO_3–ZrO_2$ catalysts were prepared by impregnation of hydrous $ZrO_2$ supplied from the Catalysis Society, Japan (JRC-ZRO-2) with aqueous anmonium metatungstate followed by calcination in air or thermal treatment in He. Pt was loaded on the $WO_3–ZrO_2$ with aqueous solution containing Pt. Hydrous $ZrO_2$ was pre-dried in air in the range 373–673 K, and impregnated with aqueous anmonium metatungstate by incipient wetness or wet-impregnation method. pH of the solution was varied from 1 to 10. The $WO_3$ loading was varied in the range 5–25 wt%. The W-impregnated $ZrO_2$ was calcined in atmospheric air in the range 923–1123 K for 2 h. Some samples were heat-treated in dry air or He stream. Platinum was loaded at 0.5 wt% with aqueous solution of $H_4PtCl_6$ or $Pt(NH_3)_4Cl_2$ followed by calcination in atmospheric air at 723 K for 2 h.

Heptane isomerization was carried out with a fixed bed flow reactor. The catalyst was pre-reduced with flowing $H_2$ at 673 K for 1 h prior to the reaction. In most of the experiments, the par-

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doi:10.1016/j.cattod.2010.10.022

tial pressures of heptane and $H_2$ were 0.047 and 0.353 MPa, and total gas flow rates were 7.46, 7.89 and 8.17 L h$^{-1}$ g-cat at 523, 553 and 573 K, respectively. Since the activity was stable with time on stream except in the initial 30 min, the reaction was performed successively in the sequence, 60 min at 573 K, 40 min at 553 K and 40 min at 523 K. The activity and selectivity were expressed by the conversion of heptane and the selectivity to branched heptanes both on C-basis.

Crystalline structures of the materials were measured by XRD for powdered samples with Rigaku Ultima III. Surface areas were measured by the BET method for $N_2$ adsorption at 77 K with Quanta Chrome Autosorb 6AG/HOB. Percents tetragonal phase of $ZrO_2$ were calculated according to Toraya et al. [13] and Ward and Ko [14].

## 3. Results

### 3.1. The stability of activity with time on stream

The catalytic activity for heptane isomerization was stable with time on stream for all catalysts examined under the reaction conditions employed. The conversions at 553 K are plotted against time on stream in Fig. 1(open circle). The conversion slightly increased in the initial 40 min of the reaction and then stayed constant for 300 min. No deactivation was observed at all. The conversions for the experiment in which the reaction temperature was changed stepwise, 573, 553, and 523 K each for 60 min are also plotted (solid circle). Except for the initial 40 min, the conversions were stable, no deactivation being observed. The conversions and selectivities at 573, 553, and 523 K were taken from the data in 60, 120, and 180 min, respectively.

Table 1 summarizes the conversions and selectivities at 573, 553, and 523 K for 21 types catalysts prepared under different preparative conditions together with surface areas, surface densities of W on the surface, and percent tetragonal for zirconia phase. Seven variables in preparative conditions are denoted by A, B, C, D, E, F, and G.

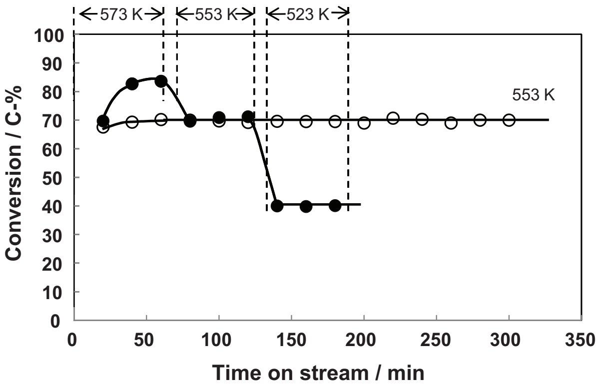

**Fig. 1.** The conversions of heptane plotted against time on stream for the reaction over $Pt/WO_3–ZrO_2$ ($WO_3$ loading 15 wt%, calcination of $WO_3–ZrO_2$ at 1053 K, catalyst No. 7 in Table 1). Open circle: reaction temperature of 553 K; total flow rate = 7.89 L h$^{-1}$ g-cat$^{-1}$; heptane pressure, 0.047 MPa; $H_2$ pressure 0.353 MPa. Solid circle: sequential change in reaction temperature; 0–60 min at 573 K, 80–120 min at 553 K, 140–180 min at 523 K.

### 3.2. Effects of pre-drying temperature of starting material hydrous zirconia

The starting hydrous zirconia (JRC-ZRO-2) was amorphous. The catalytic activity and selectivity changed with the pre-drying temperature of the hydrous zirconia. (see catalyst No. 1, 7, 16, 17 in Table 1). While pre-drying at 373, 473 and 573 K produced catalysts with almost the same activity and selectivity, pre-drying at 673 K resulted in a marked decrease in activity.

XRD patterns of hydrous $ZrO_2$ pre-dried at different temperatures are shown in Fig. 2. XRD patterns of the $Pt/WO_3–ZrO_2$ prepared from the hydrous $ZiO_2$ pre-dried at 473 K and 673 K are also included. Crystalline structures were not observed for the samples pre-dried at and below 573 K, but developed clearly for the sample pre-dried at 673 K.

**Table 1**
Preparative conditions for $Pt/WO_3ZrO_2$ and catalytic results in heptane isomerization[a].

| Cat. No. | Preparative condition | | | | | | | SA | $D_w$ | % Tetr | Conv./select. (%/%) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | A | B | C | D | E | F | G | | | | 573 K | 553 K | 523 K |
| 1 | 373 | B-1 | 4.5 | 15% | 1053 | F-1 | G-1 | 59.7 | 8.2 | | 85.1/64.0 | 72.4/83.9 | 38.6/96.1 |
| 2 | 473 | B-1 | 4.5 | 5% | 1053 | F-1 | G-1 | 39.7 | 4.1 | 1.3 | 2.5/57.9 | 1.1/43.4 | 0.4/22.0 |
| 3 | 473 | B-1 | 4.5 | 10% | 1053 | F-1 | G-1 | 57.1 | 5.7 | 23.2 | 65.8/94.0 | 42.1/94.0 | 13.3/98.0 |
| 4 | 473 | B-1 | 4.5 | 15% | 923 | F-1 | G-1 | 224 | 2.1 | 80.0 | 70.8/88.5 | 48.1/96.2 | 14.6/97.2 |
| 5 | 473 | B-1 | 4.5 | 15% | 973 | F-1 | G-1 | 91.2 | 5.4 | 79.0 | 86.8/62.3 | 75.4/83.2 | 38.8/97.0 |
| 6 | 473 | B-1 | 4.5 | 15% | 1023 | F-1 | G-1 | 81.7 | 6.0 | 76.8 | 90.2/44.8 | 80.3/72.8 | 48.5/92.5 |
| 7 | 473 | B-1 | 4.5 | 15% | 1053 | F-1 | G-1 | 61.2 | 8.0 | 55.3 | 83.6/59.5 | 71.2/86.9 | 40.1/94.1 |
| 8 | 473 | B-1 | 4.5 | 15% | 1053 | F-1 | G-2 | 60.6 | 8.0 | | 60.2/37.4 | 41.5/57.5 | 18.2/80.4 |
| 9 | 473 | B-1 | 4.5 | 15% | 1073 | F-1 | G-1 | 60.3 | 8.0 | 66.7 | 89.5/56.8 | 76.8/80.3 | 44.5/93.2 |
| 10 | 473 | B-1 | 4.5 | 15% | 1123 | F-1 | G-1 | 52.5 | 9.3 | 6.1 | 59.3/93.4 | 35.6/97.3 | 10.6/97.7 |
| 11 | 473 | B-1 | 4.5 | 15% | 1053 | F-2 | G-1 | 60.3 | 8.0 | | 82.7/60.4 | 70.9/81.7 | 40.6/95.1 |
| 12 | 473 | B-1 | 4.5 | 15% | 1053 | F-3 | G-1 | 67.7 | 7.2 | | 88.4/50.7 | 77.4/76.8 | 45.8/94.3 |
| 13 | 473 | B-2 | 4.5 | 15% | 1053 | F-1 | G-1 | 58.7 | 8.4 | | 82.0/61.1 | 67.3/80.9 | 34.3/93.9 |
| 14 | 473 | B-1 | 4.5 | 20% | 1053 | F-1 | G-1 | 59.0 | 11.1 | 63.1 | 82.0/68.8 | 67.7/87.0 | 33.0/96.4 |
| 15 | 473 | B-1 | 4.5 | 25% | 1053 | F-1 | G-1 | 44.3 | 18.5 | 71.8 | 78.3/68.8 | 62.7/86.2 | 29.3/95.4 |
| 16 | 573 | B-1 | 4.5 | 15% | 1053 | F-1 | G-1 | 56.3 | 8.7 | | 85.4/60.0 | 72.3/81.2 | 39.4/94.3 |
| 17 | 673 | B-1 | 4.5 | 15% | 1053 | F-1 | G-1 | 47.5 | 10.3 | 4.8 | 56.4/94.6 | 34.4/97.8 | 9.6/97.5 |
| 18 | Boil | B-1 | 4.5 | 15% | 1053 | F-1 | G-1 | 57.9 | 8.5 | | 82.1/61.4 | 69.2/83.2 | 37.6/95.7 |
| 19 | 473 | B-2 | 1.0 | 15% | 1053 | F-1 | G-1 | 60.6 | 8.0 | 69.8 | 81.0/71.0 | 64.6/88.4 | 29.3/97.0 |
| 20 | 473 | B-2 | 8.0 | 15% | 1053 | F-1 | G-1 | 61.1 | 8.0 | 61.0 | 87.1/60.6 | 76.1/83.2 | 43.7/96.3 |
| 21 | 473 | B-2 | 10 | 15% | 1053 | F-1 | G-1 | 63.8 | 7.7 | 66.8 | 86.4/62.8 | 74.7/84.3 | 39.6/96.2 |

A, pre-drying temperature of hydrous zirconia; B, impregnation method, incipient wetness (B-1), impregnation with dilute solution (B-2); C, pH of impregnating aqueous ammonium metatungstate; D, loading of $WO_3$ (wt%); E, calcination temperature of $WO_3–ZrO_2$ (K); F, calcination atmosphere, in static air (F-1), in flowing dry-air (F-2), in flowing He (F-3); G, Pt source, $H_4PtCl_6$ (G-1), $Pt(NH_3)_4Cl_2$ (G-2); SA, surface area (m$^2$ g$^{-1}$); $D_w$, density of W atom nm$^{-2}$; % Tetr, volume % of tetragonal phase; Conv/Select, heptane conversion (C-%)/isomerization selectivity (C-%) at indicated temperature (K).

[a] Reaction conditions: catalyst, 400 mg; heptane 0.047 MPa; $H_2$ 0.353 MPa; flow rate, heptane, 0.08 mL$_{liq}$ min$^{-1}$; $H_2$, 100 mL(STP) min$^{-1}$; total flow rate, 7.46, 7.89, and 8.17 L h$^{-1}$ g-cat$^{-1}$ at 523, 553, and 573 K, respectively.

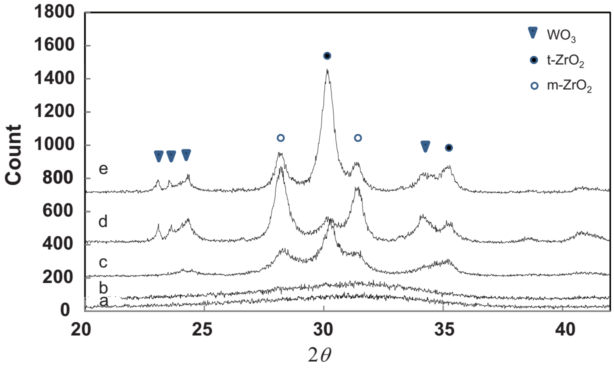

**Fig. 2.** XRD patterns of hydrous $ZrO_2$ pre-dried at different temperatures (a–c), and Pt/$WO_3$-$ZrO_2$ prepared from hydrous $ZrO_2$ pre-dried at different temperatures (d and e). Hydrous $ZrO_2$ pre-dried at 473 K (a), 573 K (b) and 673 K (c). Pt/$WO_3$–$ZrO_2$ from hydrous $ZrO_2$ pre-dried at 673 K (d) and from hydrous $ZrO_2$ pre-dried at 473 K.

The crystalline structure of the resulting Pt/$WO_3$–$ZrO_2$ was quite depending on the pre-drying temperature of the hydrous $ZrO_2$. Tetragonal phase shared 55 vol.% for the sample from hydrous $ZrO_2$ pre-dried at 473 K, while it shared 4.8% for the sample from hydrous $ZrO_2$ pre-dried at 673 K.

### 3.3. Incipient wetness and wet impregnation

The ways of impregnation, incipient-wetness and wet impregnation, also affect the activity and selectivity of the resulting catalysts to a small extent. The catalyst prepared by incipient wetness method showed slightly higher activity than the catalyst by wet impregnation (see catalyst No. 7 and 13 in Table 1).

### 3.4. Effects of pH of impregnating solution

The pH of the ammonium metatungstate solution used for wet-impregnation method exert significant effects on the activity of the resulting catalysts. As we compared catalyst No. 19, 13, 20 and 21 which were prepared with the solution of pH values 1.0, 4.5, 8.0 and 10, respectively, catalysts No. 20 and 21 showed significantly higher activity than catalysts No. 19 and 13. A high pH of the impregnating solution resulted in the catalyst of high activity, though we could not raise the pH beyond 10 because of occurrence of precipitation.

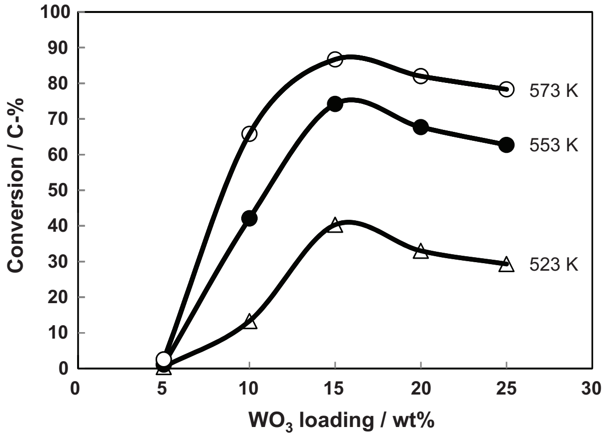

**Fig. 3.** Variation in heptane conversion over Pt/$WO_3$–$ZrO_2$ at indicated temperatures as a function of $WO_3$ loading.

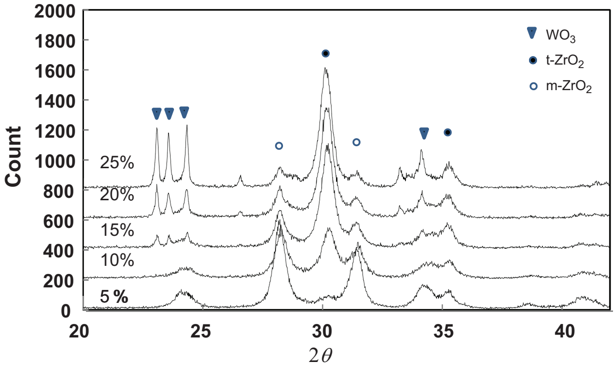

**Fig. 4.** XRD patters of Pt/$WO_3$–$ZrO_2$ catalysts with different $WO_3$ loadings indicated in wt%.

### 3.5. Effects of $WO_3$ loading

Proper $WO_3$ loading is crucial for preparation of highly active and selective Pt/$WO_3$–$ZrO_2$, which has been widely recognized. This was confirmed in the present study. The conversions are plotted against the $WO_3$ loading in Fig. 3. The catalyst containing 5 wt% $WO_3$ hardly showed activity. The activity increased with $WO_3$ loading up to 15 wt% $WO_3$ to reach a maximum activity, then decreased slightly with further increase in the $WO_3$ loading.

XRD patterns also changed significantly with $WO_3$ loading. Fig. 4 shows XRD patterns for the samples loaded with different amounts of $WO_3$. Monoclinic $ZrO_2$ was predominant over tetragonal $ZrO_2$ for the samples loaded with 5 and 10 wt% $WO_3$ loading. As the $WO_3$ loading increased, the monoclinic phase decreased and the tetragonal phase increased, attaining 71.8% tetragonal for 25 wt% $WO_3$ loaded sample. The peaks at $2\theta = 23.1°$, $23.6°$ and $24.3°$ are ascribed to crystalline $WO_3$. Crystalline $WO_3$ could not be appreciable for the samples with 5 and 10 wt% $WO_3$, but appeared for the samples with 15, 20 and 25 wt% $WO_3$.

### 3.6. Effects of calcination temperature of $WO_3$–$ZrO_2$

As reported by literature, calcination temperature of $WO_3$–$ZrO_2$ showed a strong effect on the catalytic activity of the resulting Pt/$WO_3$–$ZrO_2$. Fig. 5 shows the variations in the conversion at different reaction temperatures as a function of the calcination temperature of $WO_3$–$ZrO_2$. The activities were nearly constant for the catalysts calcined in the temperature range 973–1073 K. The

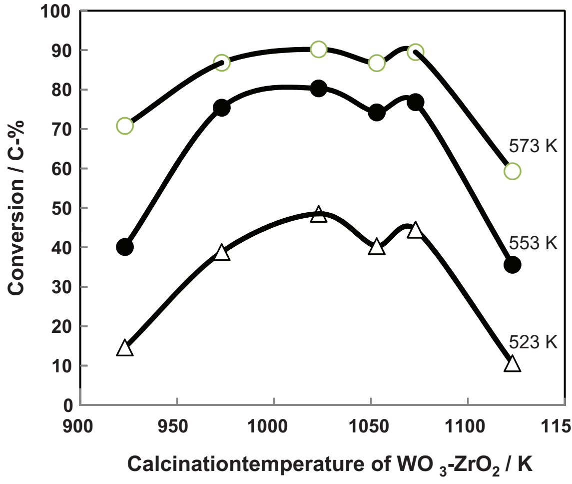

**Fig. 5.** Variation in heptane conversion over Pt/$WO_3$–$ZrO_2$ at indicated temperatures as a function of calcination temperature of $WO_3$–$ZrO_2$.

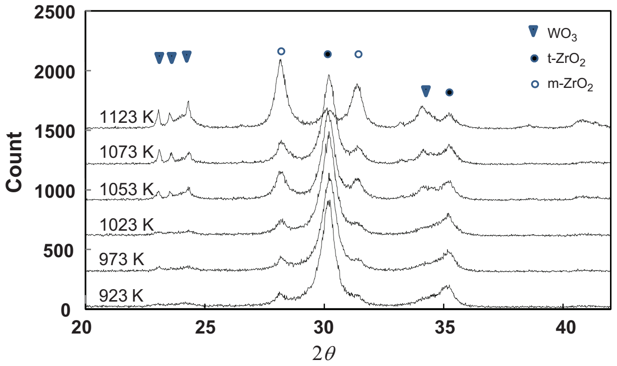

**Fig. 6.** XRD patterns of $Pt/WO_3–ZrO_2$ catalysts prepared from $WO_3–ZrO_2$'s calcined at different temperatures as indicated.

activities were significantly low for the catalyst calcined at 923 or 1123 K. The optimum calcination temperatures were in the range 973–1073 K.

Crystalline structure of $ZrO_2$ in the $Pt/WO_3–ZrO_2$ changed with calcination temperature of $WO_3–ZrO_2$. XRD patterns for the samples calcined at different temperatures are shown in Fig. 6. On calcination at 923 and 973 K, tetragonal phase shared 80 and 79%, respectively. Percent tetragonal phase decreased as the calcination temperature increased to 1073 K. A marked decrease in the % tetragonal phase was observed as the temperature increased from 1073 K to 1123 K. On calcination at 1123 K, % tetragonal phase became 6.1%. The intensities of the peaks ascribed to $WO_3$ crystallites increased with an increase in the calcination temperature.

### 3.7. *Effects of heat-treatment atmosphere*

Effects of atmosphere during calcination or heat treatment of $WO_3–ZrO_2$ were examined. The activity of the resulting $Pt/WO_3–ZrO_2$ catalyst did not change much with changing the atmosphere. Calcination in dry air flow and calcination in atmospheric static air did not make appreciable difference in the activity of the catalyst. Pre-treatment under a flowing He resulted in an increase in the activity to a small extent. The activity increased by ca. 10% when treated in He as compared to when calcined in an atmospheric air or dry air. The surface area also increased by ca. 10% for He-treated sample (see catalyst No. 7, 11, and 12 in Table 1).

### 3.8. *Effects of Pt source*

Use of $H_4PtCl_6$ and $Pt(NH_3)_4Cl_2$ as a precursor of supported Pt resulted in a different catalytic activity of the resulting $Pt/WO_3–ZrO_2$ for heptane isomerization. The catalyst prepared with $Pt(NH_3)_4Cl_2$ showed much lower activity and selectivity than that prepared with $H_4PtCl_6$. Cracking occurred to a considerable extent over the catalyst prepared with $Pt(NH_3)_4Cl_2$. The cracked products over the catalyst prepared with $Pt(NH_3)_4Cl_2$ consisted mainly of propane and isobutane which were presumed to be formed by acid-catalyzed cracking of heptane.

XRD peak that would appear at $2\theta = 39.8°$ if the Pt crystallites sufficiently large to be detected by XRD exist were not observed for both samples.

The acid amounts measured by TPD of ammonia were 0.050 mmol/g-catalyst for both catalysts (Cat. No. 7 and 8). Pt source did not affect the acid sites of the resulting catalyst.

## 4. Discussion

Heptane isomerization occurring over $Pt/WO_3–ZrO_2$ is acid-catalyzed reaction. Although acid sites are relevant to the reaction, existence of acid sites alone is not sufficient for the catalyst of high performance, in particular, in the sense of catalyst life. Mounting Pt on $WO_3–ZrO_2$ improves the catalyst life if the reaction is carried out in the presence of $H_2$. Platinum should play an important role in promoting an acid-catalyzed reaction of heptane isomerization [12]. Although the optimal states of Pt have not been clarified, the way of mounting Pt should affect the catalytic performance of the resulting $Pt/WO_3–ZrO_2$. Accordingly, optimization of the preparative variables of the catalyst includes two terms; one is optimization of the preparative variables for highly acidic $WO_3–ZrO_2$, and the other is for proper mounting of Pt on the $WO_3–ZrO_2$.

It is widely recognized that the optimal surface density of W is ca. 10 W $nm^{-2}$ which exceeds to a small extent the theoretical monolayer capacity of $ZrO_2$ (ca. 7 W atom $nm^{-2}$). A $WO_3$ loading of 15 wt% that yielded the maximum activity corresponded to a surface density of 8.0 W atom $nm^{-2}$ for the present catalysts, which is in accord with the results reported.

Effects of calcination temperature of $WO_3–ZrO_2$ on the acidity generation and catalytic activity for acid-catalyzed reaction have been extensively studied. It is well known that the calcination temperature exerts substantial effect on the acidity and catalytic activity. The optimal calcination temperature varies with the $WO_3$ loading [2], and many of the researchers calcined $WO_3–ZrO_2$ in the range 923–1173 K.

In the present study, we observed optimal calcination temperatures in the range 973–1073 K for 15 wt% $WO_3$-loaded catalyst. In our preceding paper, we reported that the optimal temperature was 1053 K for 11 wt% $WO_3$-loaded catalyst and that the catalytic activity was significantly low for the catalyst calcined at 973 K [12]. The trend that the optimal temperature was lower for the catalyst with larger loading of $WO_3$ has been reported by Barton et al. [2]. The present results together with our results obtained in our preceding paper [12] are in accord with the results reported by Barton et al. [2].

Arata and Hino reported that hydrous $ZrO_2$ should be used for impregnation with tungsten compound [11]. They showed that the activity of Pt free $WO_3–ZrO_2$ for hexane isomerization was low over the catalyst prepared from the hydrous $ZrO_2$ pre-dried at 673 K. Change in XRD has not been reported.

From Fig. 2, it is evident that hydrous $ZrO_2$ should be amorphous when impregnated with tungsten compound. Impregnation of the hydrous $ZrO_2$ pre-dried at 673 K resulted in the $Pt/WO_3–ZrO_2$ catalyst with high monoclinic phase which showed a low catalytic activity.

Selection of Pt source for mounting Pt on $WO_3–ZrO_2$ caused a great difference in the catalytic properties of the resulting $Pt/WO_3–ZrO_2$. The activity and selectivity were substantially higher for the catalyst prepared with $H_4PtCl_6$ than for the catalyst prepared with $Pt(NH_3)_4Cl_2$. In literature, $H_4PtCl_6$ was used as a Pt precursor in most cases. Other Pt compounds were also used such as $Pt(NH_3)_4(OH)_4$ [1,2], $Pt(NH_3)_4(NO_3)_2$ [5], $Pt(CH_3COO)_2$ [3], $PtCl_2$ [3], but no papers discussed the optimal selection of Pt precursor.

In $H_4PtCl_6$, Pt is in the part of anion while in $Pt(NH_3)_4Cl_2$, Pt is in the cationic part. Accordingly, it is suggested that Pt is fixed on the surface by anion exchange for $H_4PtCl_6$ but by cation exchange for $Pt(NH_3)_4Cl_2$. The anion exchange site and cation exchange site should be different on the $WO_3–ZrO_2$, and, therefore, the location of Pt should be different for the two Pt precursors.

Because the $WO_3–ZrO_2$ adsorbs both $H_2$ and CO, the difference in dispersion of Pt between the samples prepared with $H_4PtCl_6$ and $Pt(NH_3)_4Cl_2$ could not be measured by adsorption of $H_2$ or CO. We can say that Pt particles in both samples were so small that cannot be detected by XRD.

In our preceding paper, we proposed the mechanism of heptane isomerization using the concept "Molecular hydrogen-originated protonic acid site" [15] in which both Lewis acid sites and Pt par-

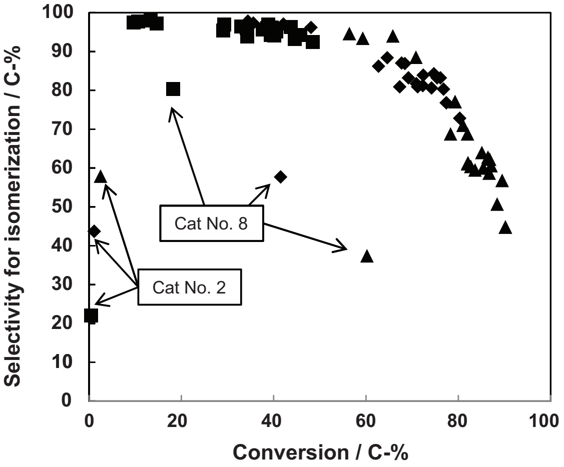

**Fig. 7.** Variations in the selectivity as a function of the conversion for all catalysts measured at 523 K (square), 553 K (diamond) and 573 K (triangle).

ticles are involved [12]. Hydrogen molecules are dissociatively adsorbed on Pt sites to form hydrogen atoms which undergo spillover onto the surface to reach Lewis acid sites where erch hydrogen atom donates an electron to Lewis acid site and becomes a proton. The proton is stabilized on the O atom adjacent to the Lewis acid site and acts as a protonic acid site. A second spiltover hydrogen atom reacts with the electron trapped by the Lewis acid site to form a hydride. As a result, a proton and a hydride are formed from a hydrogen molecule. The proton and hydride participate in the isomerization.

The location of Pt relative to Lewis acid sites and the state of Pt have not been clarified in this study, but should be different for the catalysts loaded with Pt by anion exchange and cation exchange. It is concluded that Pt should be supported on $WO_3$–$ZrO_2$ by anion exchange with Pt precursor.

It is worth noting that the effect of Pt source on the heptane isomerization was observed for Pt/zeolites system, in which use of $H_4PtCl_6$ gave a better catalyst than use of $Pt(AcAc)_2$ or $(NH_3)_4PtCl_2$ [16]. Accordingly it was commonly observed for $WO_3$–$ZrO_2$ and zeolite that supporting of Pt gave a better result by anion exchange than by cation exchange.

The activities as well as surface areas were the same for the catalysts calcined in dry air and atmospheric air. The activity was higher for the catalyst heat-treated in He than in dry air or atmospheric air. The higher activity of He treated catalyst may result from a high surface area. The presence of moisture in heat treatment did not affect the surface area, but the presence of oxygen affected. This seems to indicate that the structural change occurring heat treatment involves oxygen and not water. These results suggest that air is not necessary to be dried when $WO_3$–$ZrO_2$ is calcined.

pH of the ammonium metatungstate used for impregnation affected to a small extent the activity of the catalyst. The conversions at 553 K were 64.6, 71.2, 76.1 and 74.7% for the catalysts impregnated at pH 1.0, 4.5, 8.0 and 10, respectively (see Cat. No. 19, 13, 20 and 25 in Table 1). pH of 8.0 was the optimal impregnation condition. In literature, pH values of the impregnating solution have scarcely been described except ref. 7, where the pH of ammonium metatungstate was stabilized to be 6.0. The pH value of aqueous ammonium metatungstate was 4.5. The present results suggest that pH should be adjusted to 8 to obtain a catalyst of higher activity.

The activity of the catalyst prepared by incipient-wetness method was higher by ca. 5% than that prepared by wet impregnation method. The effect of impregnation method is appreciable but not significant as compared to the other variables examined in his study.

From the results summarized in Table 1, it can be stated that the Pt source and $WO_3$ loading exert stronger effects on the activity and selectivity of the resulting catalysts. It would be more clearly shown if the selectivities are plotted against the conversions for all catalysts examined at 523, 553 and 573 K, which is shown in Fig. 7. For reference, the equilibrium conversions are 87.7 and 85.2 at 523 and 573 K, respectively [16]. The data obtained with the catalyst prepared with $Pt(NH_3)_4Cl_2$ (Cat. No. 8) and the catalyst loaded with 5 wt% $WO_3$ (Cat. No. 2) are plotted far below the other data; both activity and selectivity were lower for the two catalysts. This indicates the enormous importance of the Pt source and $WO_3$ loading as compared with other variables in catalyst preparation.

## 5. Conclusions

1. Type of Pt source exerts substantial influence on the catalytic activity; Pt/$WO_3$–$ZrO_2$ prepared with $H_4Pt\,Cl_6$ is far better than that prepared with $Pt(NH_3)_4Cl_2$.
2. Optimum loading of $WO_3$ is ca. 15 wt% as reported by many researchers. The 15 wt% $WO_3$ corresponds to 8 W atom $nm^{-2}$.
3. Calcination of $WO_3$–$ZrO_2$ in the range 973–1073 K yields active catalysts after supporting Pt.
4. Optimal pre-drying temperature of hydrous zirconia on which tungsten compound is impregnated is in the range 373–573 K; the activity of the catalyst reduces much when the hydrous zirconia is pre-dried at and above 673 K.
5. pH of the impregnating solution of ammonium metatungstate with which hydrous zirconia is immersed affects significantly the activity of the resulting catalyst Pt/$WO_3$–$ZrO_2$; the optimum pH is ca. 8.
6. Atmosphere of heat-treatment of $WO_3$–$ZrO_3$ slightly affects the activity of the resulting catalyst Pt/$WO_3$–$ZrO_2$; heat treatment in the absence of oxygen yielded slightly better catalyst while the presence of moisture during calcination does not affect.
7. Incipient-wetness gives the catalysts of slightly higher activity than wet-impregnation.

## Acknowledgements

The authors express their appreciation to the support from the Ministry of Higher Education, Saudi Arabia in establishment of the Center of Research Excellence in Petroleum Refining and Petrochemicals (CoRE-PRP) at King Fahd University of Petroleum and Minerals (KFUPM). We are grateful to Mr. Khurshid Alam for his assistance in experimental works. H. H. wishes to thank the Japan Corporation Center, Petroleum (JCCP) for financial support under the High-level Researcher Dispatching Program, JCCP.

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