

# TUNGSTATE-MODIFIED ZIRCONIA AS A HYDROISOMERIZATION CATALYST FOR HIGH MOLECULAR WEIGHT LINEAR PARAFFINS

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**Introduction** Isomerization of long-chain linear alkanes is desirable because isoparaffins, from  $C_{10}$  to  $C_{30}$ , are excellent solvents, have minimal odor, low reactivity and high stability. They are used in polyolefin manufacture, proprietary household products, food-related applications, pharmaceutical production and in many other ways. Oils rich in high molecular weight isoparaffins, rather than normal paraffins, are desired for use as motor oils, lubricants, diesel fuel and jet fuel due to their desirable low temperature properties.<sup>1</sup> Industry carries out oil dewaxing to lower the long-chain normal paraffin content in oils. Chevron has commercialized an all-catalytic wax isomerization process, called "isodewaxing", for the production of motor oils, lubricants and fuels.<sup>2</sup> This process converts linear alkanes to their isomers whose presence significantly improves the low temperature properties of the oils. Compared with widely used solvent dewaxing, catalytic dewaxing does not have environmental problems caused by fugitive emissions.<sup>3</sup>

In the Fischer-Tropsch (FT) synthesis, the yield of waxes can exceed 45 wt% of the total liquid products.<sup>4</sup> Normal paraffins in the  $C_{20}$ - $C_{30}$  range from this process require further processing to increase their commercial value. Isomers of these high molecular weight paraffins can be used as middle-distillate fuels and their low freezing points make them desirable for use as jet fuel.<sup>5</sup> Upgrading waxes to lubricating oils is also possible.

Catalysts containing  $AlCl_3$  or zeolites are traditionally used for isomerization. The former is corrosive and nonregenerable because of loss of chloride ions; the latter requires high operating temperatures (about 400°C) and favors cracking. SAPO-11 (a silicoaluminophosphate) is a relatively new molecular sieve; metal-promoted SAPO-11 is more selective than other zeolites for long-chain paraffin isomerization.<sup>6,7</sup> However, it is generally used with high hydrogen to feed mole ratios (30/1) and high reaction temperatures.

Anion-modified metal oxides, such as sulfated zirconia ( $SO_4/ZrO_2$ ) and tungstated zirconia ( $WO_3/ZrO_2$ ), have been found to catalyze hydrocarbon conversions under mild conditions.<sup>8</sup> These strong solid acids are environmentally benign and regenerable.<sup>9</sup> Butane isomerization over sulfated zirconia has attracted considerable attention because isobutane is the precursor to methyl-t-butyl ether.<sup>10-13</sup> Metal-promoted sulfated zirconia is effective for isomerization of short chain paraffins ( $< C_7$ ) and for hydrocracking of long-chain paraffins including waxes and polyolefins.<sup>14-16</sup> However, loss of activity due to coke formation and sulfur loss, especially under reducing conditions, are obstacles to certain practical uses of sulfated zirconia. Moreover, high isomerization selectivity is difficult to achieve over sulfated zirconia as the chain length increases, even at low conversions.<sup>15</sup> Studies of tungstate-modified zirconia indicate that it is more stable than sulfated zirconia and is promising for hydroisomerization of high molecular weight linear paraffins.<sup>16-20</sup>

It is known that there is an increasing ease of formation of carbenium ions on the interior carbons of linear molecules of long chains.<sup>21</sup> Since isomerization of alkanes precedes cracking, catalysts with a certain optimal balance of metal and acid functions at suitable reaction conditions must be found to suppress cracking in order to achieve high isomerization selectivity for long-chain paraffins.<sup>7,22,23</sup> Although these reactions proceed via carbenium ions, initiation of these species and subsequent reaction pathways on anion-modified zirconia catalysts are still unclear.<sup>24,25</sup>

This study contributes to investigation of hydroisomerization of high molecular weight linear alkanes over metal-promoted tungstate-modified zirconia (metal/ $WO_3/ZrO_2$ ), using n-hexadecane as a model compound in a trickle bed reactor. Efforts are aimed at obtaining high hydroisomerization selectivity with high hydrocarbon conversion and at elucidating reaction pathways over this class of anion-modified metal oxide.

## Experimental

**Catalyst Preparation and Characterization** The procedure for synthesis of metal/ $WO_3/ZrO_2$  consists of the following steps: (1) zirconium hydroxide precipitation by addition of ammonium

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hydroxide to zirconium chloride; (2) anion-modification by addition of ammonium metatungstate solution; (3) impregnation of a metal (Pt, Pd, or Ni) salt; (4) calcination. Two preparation procedures (labeled I and II in Figure 1) were used. In I, there were two calcinations, one at 700°C for tungstate-modified zirconium hydroxide and the other at 500°C after metal salt impregnation; procedure II had only one calcination at 700°C after co-impregnation of zirconium hydroxide by the solution of tungsten and metal salts. The metal content and tungsten content in the catalysts were controlled by adjusting the concentration of salts. In this paper, the metal salt we used is  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ . Figure 1 shows details of procedures I and II.

BET specific surface area (by nitrogen adsorption) and platinum distribution (by carbon monoxide adsorption) were measured using a Micromeritics ASAP 2010 instrument.

**Reactor System and Operating Procedure** Catalytic activity and selectivity tests were carried out in a continuous trickle bed stainless steel reactor with 0.305 inch i.d. Reaction temperature was controlled by a computer and system pressure by a back-pressure valve.  $n\text{-C}_{16}$  (99 wt% from ICN Biomedical Inc.) was delivered from a feed tank into the reactor by a syringe pump at a constant rate of 6.6 ml/hr. Input rates of hydrogen and helium (make-up gas to keep gas flow rate constant when studying effects of pressure) were controlled by two mass flow meters, respectively. The catalyst was crushed to 40-60 mesh pellets and placed into the center of the reactor after mixing with an equal volume of quartz (50-70 mesh). Quartz was also used as packing at each end of the reactor. Variation in weight hour space velocity (WHSV) was obtained by changing the amount of catalyst. Before reaction, the catalyst was activated at 450°C with 20 ml/min of air for one hr. Liquid products were collected in an ice-water cooled vial for analysis using an HP-5980 GC.

**Results and Discussion**  $n\text{-C}_{16}$  conversion is defined as the difference between  $n\text{-C}_{16}$  weight percentage in the feed and that in the reaction products;  $i\text{-C}_{16}$  selectivity is calculated by dividing  $i\text{-C}_{16}$  percentage in the products with  $n\text{-C}_{16}$  conversion;  $i\text{-C}_{16}$  yield is the  $i\text{-C}_{16}$  percentage. In order to obtain comparable  $n\text{-C}_{16}$  conversion with different catalysts, we carried out the activity and selectivity tests at 300°C. Later, the possibility of operating reactions at lower temperatures, from 210 to 250°C, using our most active catalyst (6.5 wt% W) was investigated and the influence of reaction pressure was studied at 230°C.

**Comparison of results from catalysts prepared by methods I and II** These two  $\text{Pt}/\text{WO}_3/\text{ZrO}_2$  catalysts, I and II, with the same composition (0.5 wt% platinum and 6.5 wt% tungsten) were tested under the same conditions but at varying WHSV: 300°C, 300 psig,  $\text{H}_2/n\text{-C}_{16}$  (mole ratio)=2. Results are shown in Figure 2.  $n\text{-C}_{16}$  conversion decreases and  $i\text{-C}_{16}$  increases for both catalysts when WHSV increases, but the  $n\text{-C}_{16}$  conversion with catalyst II declines more rapidly. At the same  $n\text{-C}_{16}$  conversion, 90 wt%, for instance, the  $i\text{-C}_{16}$  selectivity over catalyst I is about 20 wt% higher than that over catalyst II. A possible explanation is that the high temperature calcination (700°C) after platinum salt impregnation used in procedure II resulted in a low degree of platinum distribution and the metal function is weakened. These two catalysts have similar surface areas, about 67.5  $\text{m}^2/\text{g}$ , but carbon monoxide chemisorption experiments show platinum distribution of catalyst I is 0.63, which is much better than that of II (0.14). It is known that metals, such as platinum, palladium or nickel, can provide hydride ions<sup>26</sup> and enhance acidity by hydrogen spillover in the presence of hydrogen<sup>27</sup>. Lack of available hydride ions may result in long residence times for reaction intermediates and increase the opportunity for  $\beta$ -scission which produces cracked products.

**Effect of tungsten content on catalyst reactivity** Five  $\text{Pt}/\text{WO}_3/\text{ZrO}_2$  catalysts with different tungsten contents but the same amount of platinum content (0.5 wt%) were prepared by method I. Properties are shown in Table 1. These catalysts were tested at the same temperature, pressure and hydrogen to  $n\text{-C}_{16}$  ratio (Figure 2). Catalysts with 6.5 and 8 wt% tungsten have high hydroisomerization activities at relatively high conversion. Data from BET nitrogen adsorption measurement indicates the surface area of  $\text{Pt}/\text{WO}_3/\text{ZrO}_2$  increases with increasing tungsten content. It has been postulated that tungsten oxide is reduced in the presence of hydrogen; the reduced species may play an important part in the reaction mechanism.<sup>28</sup> Surface density and particle size of tungsten oxide as well as acidity will be studied by TEM, XPS and TPD.

**Effect of reaction temperature and pressure** Influence of reaction temperature and pressure on conversion and isomerization selectivity was investigated using a  $\text{Pt}(0.5 \text{ wt}\%)/\text{WO}_3/\text{ZrO}_2$  (6.5 wt% W) catalyst prepared by procedure I. Data in Tables 2 and 3 indicates that  $n\text{-C}_{16}$  conversion and  $i\text{-C}_{16}$  selectivity are more sensitive to reaction temperature than to pressure. In the temperature range from 210 to 250°C, lowering the temperature resulted in low conversion but high selectivity. This catalyst is very active; 85.9 wt%  $n\text{-C}_{16}$  conversion with 83.1 wt%  $i\text{-C}_{16}$  selectivity was achieved at 230°C,  $\text{WHSV} = 1 \text{ hr}^{-1}$ . Comparable  $n\text{-C}_{16}$  conversion (82.8 wt%) was

also obtained at higher temperature and larger WHSV (300°C, WHSV=24 hr<sup>-1</sup>, line C in Figure 3), but the i-C<sub>16</sub> selectivity was only 74.3 wt%. This suggests that large i-C<sub>16</sub> yields will be obtained at relatively low temperature and small WHSV, rather than high temperature and large WHSV. The increase of pressure resulted in low conversion with high selectivity, indicating a negative reaction order of hydrogen. A similar effect of hydrogen on conversion was observed by Iglesias *et al.* in heptane isomerization using Pt/WO<sub>3</sub>/ZrO<sub>2</sub>.<sup>26</sup>

**Comparison of Pt(0.5 wt%)/SO<sub>4</sub>/ZrO<sub>2</sub> and Pt(0.5 wt%)/WO<sub>3</sub>/ZrO<sub>2</sub>** At relatively low temperature (150°C), platinum-promoted sulfated zirconia (calcined at 630°C for 3 hr in air) was tested for n-hexadecane hydroisomerization. Its preparation procedure is described elsewhere.<sup>14</sup> Results with Pt(0.5 wt%)/SO<sub>4</sub>/ZrO<sub>2</sub> are compared with those obtained using Pt(0.5 wt%)/WO<sub>3</sub>/ZrO<sub>2</sub> (6.5 wt% W) in Table 4. Pt(0.5 wt%)/SO<sub>4</sub>/ZrO<sub>2</sub> is active at 150°C, but it favors cracking. Pt(0.5 wt%)/WO<sub>3</sub>/ZrO<sub>2</sub> requires higher temperature, but has high isomerization selectivity even at high hexadecane conversion.

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## REFERENCES

1. Encyclopedia of Chemical Processing and Design, 15, Mcketta, M., Dekker, M., Inc. (1982).
2. Miller, S. J., Studies in Surface Science and Catalysis, Vol. 84 (1994), pp. 2319-2326.
3. Kim, I., Chem. Eng., Dec. 1995, pp. 71.
4. Encyclopedia of Chemical Technology, Fourth Edition, Vol. 12 (1996).
5. Coppola, E. N., M. S. thesis, University of Utah (1987).
6. Miller, S. J., preprints of Div. Petrochem., Am. Chem. Soc., 38 (1993), pp. 788-793.
7. Taylor, R. J., Pretty, R., Appl. Catal. A 119 (1994), pp. 121-138.
8. Hino, M. and Arata, K., J. Am. Chem. Soc., 101 (1979), pp. 39-40.
9. Yori, J. C., Luy, J. C. and Parera, J. M., Appl. Catal. 46 (1989), pp. 102-112.
10. Corma, A., Juan-Rajadell, M. I., Lopez-Nieto, J. M., Martinez, A., Martinez, C., Appl. Catal. A 111 (1994), pp. 175-189.
11. Yori, J. C., Parera, J. M., Appl. Catal. A 129 (1995), pp. 83-91.
12. Arata, K., Appl. Catal. A 146 (1996), pp. 3-32.
13. Liu, H., Lei, G. D., Sachtler, W. M. H., Appl. Catal. A 146 (1996), pp. 165-180.
14. Wen, M. Y., Wender, I., Tierney, J. W., Energy & Fuels, 4 (1990), pp. 372-379.
15. Keogh, R. A., Sparks, D., Hu, J., Wender, I., Tierney, J. W., Wang, W., and Davis, B. H., Energy & Fuels, 8 (1994), pp. 755-762.
16. Venkatesh, K. R., Hu, J., Wang, W., Holder, G. D., Tierney, J. W., and Wender, I., Energy & Fuels, 10 (1996), pp. 1163-1170.
17. Chang, C.D., Santiesteban, J. G., Stern, D. L., U.S. Patent 5,345,026 (1994).
18. Soled, S. L., Gates, W. E., Iglesia, E., U.S. Patent 5,422,327 (1995).
19. Larsen, G., Lotero, E., Raghavan, S., Prira, R. D., Querini, C. A., Appl. Catal. A 139 (1996), pp. 201-211.
20. Iglesia, E., Barton, D. G., Soled, S. L., Miseo, S., Baumgartner, J. E., Gates, W. E., Fuentes, G. A., and Meitzner, G. D., Stud. Surf. Sci. and Catal., Vol. 101 (1996), pp. 533-542.
21. Corma, A. and Wojciechowski, B. W., Catal. Rev.-Sci. Eng., 27(1) (1985), pp. 83.
22. Weitkamp, J., Jacobs, P. A. and Martens, J. A., Appl. Catal. 8(1983), pp. 123-141.
23. Girgis, M. J. and Tsao, Y. P., Ind. Eng. Chem. Res., 35 (1996), pp. 386-396.
24. Farcasiu, D., Ghenciu, A., and Li, J. Q., J. Catal., 158 (1996), pp. 116-127.
25. Parera, J. M., Appl. Catal. A 167 (1998), pp. 75-84.
26. Iglesia, E., Soled, S. L., and Karmer, G. M., J. Catal., 144 (1993), pp. 238-253.
27. Shishido, T., Hattori, H., Appl. Catal. A 146 (1996), pp. 157-164.
28. Larsen, G., Lotero, E., and Parra, R., Stud. Surf. Sci. and Catal., Vol. 101 (1996), pp. 543-551.

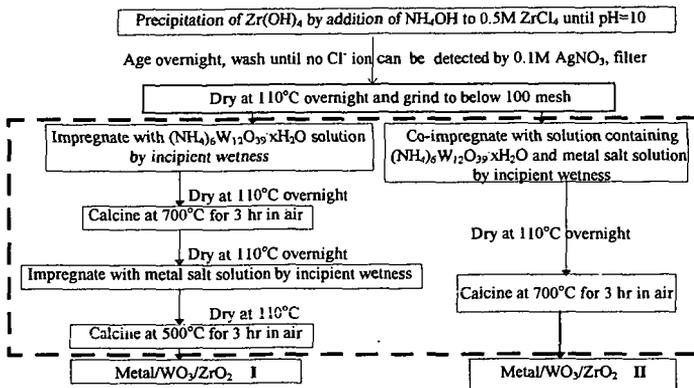


Figure 1 Two procedures for the preparation of Metal/ $WO_3/ZrO_2$  catalysts

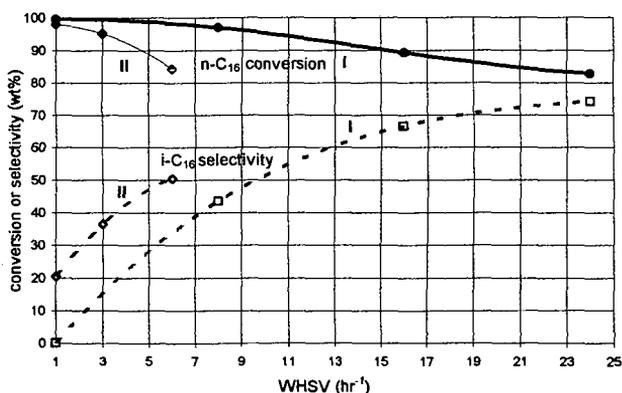


Figure 2 Comparison of conversion and selectivity for hydroisomerization of  $n-C_{16}$  using  $Pt(0.5wt\%)/WO_3/ZrO_2$  (6.5 wt% W) catalysts prepared by procedures I and II. [Reaction conditions: 300°C, 300 psig,  $H_2/n-C_{16}$ (mole ratio)=2, 6th hr reaction results]

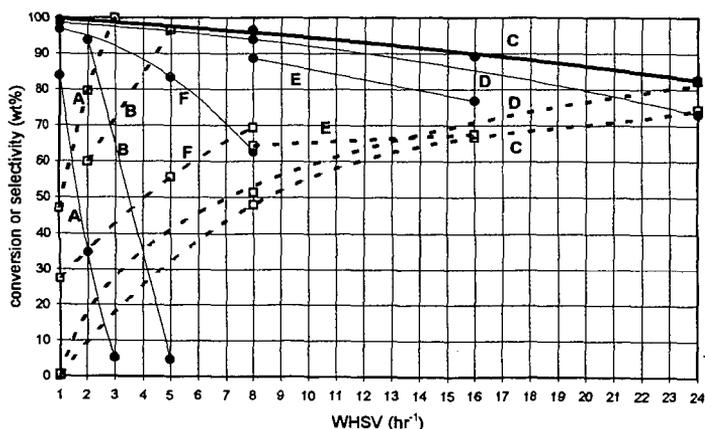


Figure 3 Effect of tungsten content in  $Pt(0.5wt\%)/WO_3/ZrO_2$  on  $n-C_{16}$  conversion (—) and  $i-C_{16}$  selectivity (----) [catalysts prepared by procedure I; reaction conditions: 300°C, 300 psig,  $H_2/n-C_{16}$  (mole ratio)=2, 6th hr results]

Table 1 Physical properties of Pt(0.5 wt%)/WO<sub>3</sub>/ZrO<sub>2</sub> with different tungsten contents

catalyst	A	B	C	D	E	F
W wt%	3	4.5	6.5	8	10	15
surface area m <sup>2</sup> /g	42.46	56.4	67.49	74.87	90.01	99.10
pore diameter Å	125.1	111.8	96.8	88.2	87.3	72.5
pore volume cm <sup>3</sup> /g	0.14	0.16	0.16	0.16	0.20	0.18

Table 2 Effect of reaction temperature on n-C<sub>16</sub> conversion and i-C<sub>16</sub> selectivity over Pt(0.5 wt%)/WO<sub>3</sub>/ZrO<sub>2</sub> (6.5 wt% W) by procedure I

reaction temperature °C	210	220	230	250
n-C <sub>16</sub> conversion, wt%	33.5	53.8	85.9	98.3
i-C <sub>16</sub> selectivity, wt%	99.1	96.6	83.1	0
i-C <sub>16</sub> yield, wt%	33.2	52.0	71.4	0
i-C <sub>16</sub> distribution wt%				
multibranch i-C <sub>16</sub>	5.4	10.7	26.6	0
dimethyltetradecane	31.3	36.6	42.8	0
7- and 8-methylpentadecane	15.1	11.8	6.4	0
6-methylpentadecane	13.0	10.8	5.8	0
5-methylpentadecane	9.9	8.2	4.6	0
4-methylpentadecane	8.7	7.3	4.0	0
3-methylpentadecane	8.7	7.5	4.6	0
2-methylpentadecane	6.3	5.9	4.0	0
3-ethyltetradecane	1.5	1.2	0.8	0

Reaction conditions: 300 psig, H<sub>2</sub>/n-C<sub>16</sub> (mole ratio)=2, WHSV= 1 hr<sup>-1</sup>Table 3 Effect of reaction pressure on n-C<sub>16</sub> conversion and i-C<sub>16</sub> selectivity over Pt(0.5 wt%)/WO<sub>3</sub>/ZrO<sub>2</sub> (6.5 wt% W) by procedure I

reaction pressure	300	400	500	600
n-C <sub>16</sub> conversion, wt%	85.9	78.8	76.1	70.7
i-C <sub>16</sub> selectivity, wt%	83.1	88.9	90.7	93
i-C <sub>16</sub> yield, wt%	71.4	70.1	69.1	65.8
i-C <sub>16</sub> distribution wt%				
multibranch i-C <sub>16</sub>	26.6	20.0	19.9	17.2
dimethyltetradecane	42.8	43.2	41.5	40.5
7- and 8-methylpentadecane	6.4	8.0	8.8	9.3
6-methylpentadecane	5.8	7.0	7.0	8.2
5-methylpentadecane	4.6	5.7	6.0	6.6
4-methylpentadecane	4.0	4.8	5.4	5.9
3-methylpentadecane	4.6	5.3	5.6	6.1
2-methylpentadecane	4.0	4.6	4.7	5.0
3-ethyltetradecane	0.8	1.0	1.0	1.1

Reaction conditions: 230°C, H<sub>2</sub>/n-C<sub>16</sub> (mole ratio)=2, WHSV= 1 hr<sup>-1</sup>Table 4 Comparison of Pt(0.5wt%)/SO<sub>4</sub>/ZrO<sub>2</sub> (630°C) and Pt(0.5wt%)/WO<sub>3</sub>/ZrO<sub>2</sub> [6.5wt% W (700, 500°C)]

Catalyst	Pt(0.5 wt%)/SO <sub>4</sub> /ZrO <sub>2</sub> (630°C)	Pt(0.5 wt%)/WO <sub>3</sub> /ZrO <sub>2</sub> 6.5 wt% W (700, 500°C)
Reaction conditions	150°C, 300 psig, WHSV=1hr <sup>-1</sup>	230°C, 300 psig, WHSV=1hr <sup>-1</sup>
n-C <sub>16</sub> conversion, wt%	76.7	85.9
i-C <sub>16</sub> selectivity, wt%	19.8	83.1
i-C <sub>16</sub> yield, wt%	15.2	71.4
i-C <sub>16</sub> distribution wt%		
multibranch i-C <sub>16</sub>	21.2	26.6
dimethyltetradecane	44.3	42.8
monomethylpentadecane	33.6	29.4
3-ethyltetradecane	0.6	0.8