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Effect of the Cr_2O_3 Promoter on $\text{Pt}/\text{WO}_3\text{-ZrO}_2$ Catalysts for n-Heptane Isomerization

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Abstract: Isomerate, the product of a light naphtha Isomerization unit, is a clean, high-octane gasoline blending component, which is free of sulfur content, aromatics, and olefins. However, the isomerization of the long-chain alkanes, such as n-heptane, is pretty difficult. As a result, this process has not been commercialized yet. In recent years, much attention has been paid to $\text{Pt}/\text{WO}_3/\text{ZrO}_2$ as an n-heptane isomerization catalyst due to its good thermal stability, strong acidity, simplicity of preparation, reusability and good isomerization activity. In this work, the $\text{Pt}/\text{WO}_3/\text{ZrO}_2$ catalyst was modified by various loading of metal Cr to improve the catalytic performance. The effects of WO_3 content, Cr metal loading and calcination temperature on the catalyst characters and catalytic activity were studied. It is shown that Cr-Pt/ WO_3/ZrO_2 with the loading of 18 wt% WO_3 and 1.0–1.4 wt% Cr, prepared at the calcination temperature of 800 °C, has the highest activity. It was found that the octane number increases by 28 units through the isomerization of light naphtha feedstocks. In addition, the study on the stability of Cr-Pt/ WO_3/ZrO_2 indicates that the catalyst is not deactivated after 500 h of the n-heptane isomerization reaction.

Keywords: Solid superacid; $\text{Pt}/\text{WO}_3/\text{ZrO}_2$; n-heptane; hydrogen isomerization; Cr

1. Introduction

Current stringent environmental protection regulations have forced the implementation of severe controls for reducing aromatic, olefin, and sulfuric compounds and led to a sharp rise in the demand for clean fuels with none-aromatic and high octane number [1,2]. Heptane isomerization to branched isomers with high octane numbers is a desirable reaction for compensating for the octane number [3,4]. However, no process that is suitable for heptane fraction isomerization in industrial oil refining is currently known; since the implementation of such a process will allow for the meeting of long-term environmental requirements for commercial gasoline, it has aroused increased interest [4]. The main concern for the commercialization of n-heptane isomerization is that β -cleavage occurs during the isomerization reaction. A suitable catalyst needs to be developed to prevent n-heptane from cracking while promoting the conversion of n-heptane to multi-branched isomers [5].

$\text{SO}_4^{2-}/\text{ZrO}_2$ catalysts have attracted significant attention because of their ability to isomerize light alkanes at low temperature, but suffer from the disadvantages of deactivation and possibly from sulfur loss during reaction and regeneration, limiting their applicability in isomerization. As an alternative to $\text{SO}_4^{2-}/\text{ZrO}_2$, WO_3/ZrO_2 has become increasingly important since its discovery by

Arata and Hino [6] because of its good stability both in reducing and oxidizing conditions [7]. While the WO_3/ZrO_2 type catalyst shows high selectivity in the isomerization reaction of linear alkane, the catalyst activity is relatively low and the degree of cracking is too high [8]. Thus, the catalyst needs to be modified to meet the industrial production requirements. The catalyst consisting of Pt deposited on WO_3/ZrO_2 for n-heptane isomerization has attracted the attention of a large number of researchers as the most promising catalyst [9,10]. The structure of the WO_3/ZrO_2 catalyst varies depending on the WO_3 content [11,12], leading to different catalyst activities. The structure and properties of this kind of catalyst can be modified by changing the WO_3 content [13]. While most researchers believe that the best catalytic activity is obtained when WO_3 is highly dispersed on the surface of the catalyst, there has been some debate about this subject. It was shown that the catalyst has better catalyst activity with the WO_3 density of seven–eight atoms·nm^{−2} [14,15]. Many researchers have found that the addition of small amounts of metals such as Fe, Al, In, and Ga to Pt/ WO_3/ZrO_2 enhances catalysis and stability of n-heptane isomerization, and it was demonstrated that Cr can be used as a modifier in Pt/ WO_3/ZrO_2 catalysts. Based on economic considerations, Cr metal is a more cost-effective option, and is therefore a more suitable for industrial production than Ga metal [16–18]. In this work, n-heptane isomerization over Cr-promoted Pt/ WO_3/ZrO_2 was studied and compared to that over Pt/ WO_3/ZrO_2 .

2. Results and Discussion

2.1. Effect of Cr_2O_3 Loading on Pt/ WO_3/ZrO_2

2.1.1. Characterization of the Catalysts

The XRD patterns of Cr-Pt/WZ catalysts with different Cr loading are presented in Figure 1. All of the catalysts show a mixture of the tetragonal and monoclinic zirconia phases, while they are dominated by the tetragonal phase. The Cr-Pt/WZ catalyst exhibits lower diffraction peak intensities of monoclinic ZrO_2 than the Pt/WZ catalyst. The intensities of the diffraction peaks of the tetragonal ZrO_2 phase increase at first and then decrease with increasing of Cr loading. This result shows that the appropriate amount of Cr incorporation helps to stabilize the tetragonal ZrO_2 phase of the Pt/WZ catalysts and inhibits the transformation from the tetragonal phase to the monoclinic phase during calcination at high temperature, leading to higher isomerization activity [19]. The peaks of crystalline WO_3 almost disappear when the Pt/WZ catalysts were loaded with Cr. The interaction between Cr and WO_3 reduces the energy of crystalline WO_3 on the surface of the catalyst, promoting the dispersion of WO_3 . Based on the experiments, the optimal Cr content is 1.0–1.4 wt%.

Figure 1. XRD patterns of the Cr-Pt/WZ catalyst with different Cr contents.

The specific surface area, pore size and volume of the Pt/WZ samples with different Cr contents were characterized using BET analysis, and the results are presented in Table 1. The addition of Cr changes the specific surface areas of WZ. It is shown that the optimal Cr content of approximately 1.0 wt% results in larger pore diameter and specific surface area, which in turn leads to more active sites and acid sites [20]. Thus, the Cr-Pt/WZ catalyst will become more active in n-heptane isomerization. The result also shows that Cr can improve the pore structure of the catalysts, but the dispersed oxides will be found in the pores of Pt/WZ as the Cr content increases.

Table 1. The specific surface area and pore size and volume of the Cr-Pt/WZ catalysts with different Cr contents.

Sample	$S_{BET}/(m^2 \cdot g^{-1})$	$V_P/(cm^3 \cdot g^{-1})$	d_p/nm
Pt/WZ	77.06	0.153	6.54
0.2 wt% Cr-Pt/WZ	80.94	0.161	6.53
0.6 wt% Cr-Pt/WZ	105.26	0.168	6.14
1.0 wt% Cr-Pt/WZ	103.5	0.177	6.85
1.4 wt% Cr-Pt/WZ	92.94	0.163	5.84
1.8 wt% Cr-Pt/WZ	89.94	0.161	5.83

The surface acidity of the catalyst was characterized by NH_3 -TPD. The effect of Cr loading on the catalyst acidity was studied. As shown in Figure 2, the area of the desorption peaks at 350 °C and 650 °C increase at first and then decrease with the increase of the Cr content, indicating that the medium-strong acid sites and superacid sites on the catalyst increase at first and then decrease. The Cr-Pt/WZ catalyst with 1.0 wt% Cr has the most acidic sites. As a result, it has the greatest isomerization activity [21].

Figure 2. NH_3 -TPD curves of the Cr-Pt/WZ catalyst with different Cr contents.

2.1.2. Catalytic Activity of the Catalysts

As shown in Figure 3, the reaction temperature has a great influence on the activity of the catalyst. The conversion of n-heptane gradually increases with the increase of reaction temperature, indicating the increases of the isomerization rate. However, the isomerization equilibrium constant K_p decreases, which is unfavorable to the isomerization rearrangement reaction. At the same time, the rate of the cracking is promoted when the temperature increases because cracking is an endothermic reaction.

A comprehensive analysis shows that the yield of isomeric heptane is relatively high, and products have a higher proportion of multi-branched isomers at the reaction temperature of approximately 220 °C, which leads to a higher octane number.

Figure 3. The activity of Cr-Pt/WZ catalysts with different Cr content. Reaction condition: $n(\text{H}_2):n(\text{C}_7) = 9 \text{ mol/mol}$, LHSV(liquid hourly space velocity) = 0.7 h^{-1} , and $P = 1.0 \text{ MPa}$, $T = 200\text{--}280 \text{ }^\circ\text{C}$. S-Yield: Single-chain isomer yield, M-Yield: Multi-branched isomer yield, M/S: M-Yield/ S-Yield.

At the reaction temperature of 220 °C, the yield of isomeric heptane increases at the beginning and then decreases as the Cr content increases. When the Cr content increases from zero to 1.0 wt%, the isomeric heptane yield increases from 40.5% to 73.7%. Further increase of the Cr content to 1.4 wt% does not bring an apparent yield change. Upon an increase to 1.8 wt%, the yield decreases to 68.9%. Based on Figure 1, the peak intensity of the tetragonal ZrO_2 phase that endows the catalyst with its catalytic activity is the strongest, and the catalyst has the strongest acidity and reduction ability, resulting in the best catalytic activity.

2.2. Effect of WO_3 on Pt/WZ

2.2.1. Characterization of the Catalysts

The XRD pattern of the Cr-Pt/WZ catalyst is shown in Figure 4. It is known that a characteristic WO_3 peak cannot be observed when its content is lower than 18 wt% because WO_3 is highly dispersed on the surface of the catalyst and no WO_3 crystals are formed. WO_3 exists on the surface of the catalyst due to the stable W-O-Zr bonding [21]. W-O-Zr bonding prevents the tetragonal ZrO_2 from transforming to a monoclinic one. It can be observed in Figure 3 that the catalyst with 18 wt% WO_3 has a stronger diffraction intensity of tetragonal ZrO_2 and a weaker diffraction intensity of WO_3 . Thus, it will form a relatively stable solid superacid structure resulting in a higher catalyst activity at a lower temperature.

Figure 4. XRD patterns of the Cr-Pt/WZ catalysts with different WO_3 contents.

The specific area, pore size, and volume of the Pt/WZ samples with different WO_3 contents were analyzed, and the results are presented in Table 2. The results show that the catalyst with approximately 15 wt% WO_3 has a relatively large pore diameter and higher specific surface area. The highly dispersed WO_3 on the surface of the catalyst prevents the catalyst from agglomeration at high temperatures [22]. In addition, WO_3 can also increase the exposed structure of the catalyst, resulting in a high specific surface area. However, as the WO_3 content increases, the WO_3 is found as coke deposition and forms the WO_3 crystal. The WO_3 crystals are dispersed in the catalyst channel, leading to the reduction of the catalyst specific surface area. The specific surface area of the Cr-Pt/WZ decreases when the content of WO_3 increased to 24 wt%.

Table 2. The specific surface area and pore size and volume of the Cr-Pt/WZ catalyst with different WO_3 contents.

Sample	$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$	$V_P/(\text{cm}^3 \cdot \text{g}^{-1})$	$d_P/(\text{nm})$
Cr-Pt/12 wt%WZ	102.8	0.180	6.86
Cr-Pt/15 wt%WZ	128.3	0.182	6.90
Cr-Pt/18 wt%WZ	103.5	0.177	6.85
Cr-Pt/21 wt%WZ	89.54	0.166	6.42
Cr-Pt/24 wt%WZ	75.21	0.124	6.57

The surface acidity of the catalyst was characterized by NH_3 -TPD, and the effect of WO_3 loading on the catalyst acidity was studied. The results are shown in Figure 5. The desorption peak area of NH_3 at 350 °C increases at first and then decreases with the increase in WO_3 content, indicating that the medium-strong acidic sites increased at first and then decreased. The Cr-Pt/WZ catalyst has the most acidic sites when the WO_3 content is 18–21 wt%, and therefore, the catalyst has the greatest isomerization activity. However, the desorption peak area of NH_3 at 650 °C increases with the increase of WO_3 content, implying that the superstrong acid sites increase with WO_3 content increasing. An appropriate WO_3 content prevents the transformation of ZrO_2 from the tetragonal phase to the monoclinic phase. As a result, it increases the acidity of the catalyst, resulting in a higher activity. However, with the increase in WO_3 content, the WO_3 on the surface of the catalyst aggregates and blocks the acidic sites of the catalyst. Thus, the activity of the catalyst decreases due to the decrease of the acid sites number on the catalyst. This is approved by the results of the XRD and BET characterizations.

Figure 5. NH_3 -TPD curves of the Cr-Pt/WZ catalyst with different WO_3 contents.

2.2.2. Catalytic Activity of the Catalysts

The performance of the Cr-Pt/WZ catalyst with 12–24 wt% WO_3 was evaluated and the results are shown in Figure 6. It can be observed that the isomer yield of n-heptane increases at the beginning and then decreases with the increase of the WO_3 content. At the reaction temperature of 220 °C, the isomer yield of n-heptane increases to 73.7% when the WO_3 content increases to 18 wt%. However, the isomer yield of n-heptane decreases sharply when the WO_3 content increases further. According to the XRD characterization and the state diagram of WO_x on the WO_3/ZrO_2 surface [23], the catalyst is in the growth zone of tungstate when the loading of WO_3 is 12–18 wt%. The catalyst activity increases as the WO_3 content increases in this range. Then, the catalyst is found in the tungstate and WO_3 region when the WO_3 content is 24 wt%. As a result, the catalyst activity decreases. When the WO_3 content was 12 wt%, and no WO_3 peak was observed in the catalyst sample, the formation of the monoclinic ZrO_2 phase was not well suppressed, and the catalytic activity was low. The characteristic peak of WO_3 begins to appear in the catalyst, and the characteristic peak of the monoclinic ZrO_2 phase is weak for the WO_3 content of 18 wt%. In this case, WO_3 on the catalyst surface effectively prevents the conversion of the tetragonal ZrO_2 phase to the monoclinic phase. The tetragonal ZrO_2 has a large specific surface area, forming more acidic sites, and tetragonal ZrO_2 acts a solid superacid structure so that the catalyst has strong activity.

Figure 6. The activity of the Cr-Pt/WZ catalysts with different WO_3 contents. Reaction condition: $n(\text{H}_2):n(\text{C}_7) = 9 \text{ mol/mol}$, $\text{LHSV} = 0.7 \text{ h}^{-1}$, and $P = 1.0 \text{ MPa}$, $T = 200\text{--}280 \text{ }^\circ\text{C}$.

2.3. Effect of Calcination Temperature on Catalyst Activity

The calcination temperature is an important factor affecting the degree of reduction and dispersion of the WO_3 over the WO_3/ZrO_2 catalyst. A suitable calcination temperature is a prerequisite for preparing a high activity catalyst. A suitable calcination temperature is generally considered to be between 600 and 900 °C.

2.3.1. Characterization of the Catalysts

The TG-DTA curves of Pt/WZ precursor catalyst are shown in Figure 7. The endothermic peak of the DTA curve between 100 and 300 °C is attributed to the removal of adsorbed water and crystalline water from the catalyst surface. The weight loss rate of the catalyst is greater below 200 °C, mainly due to the removal of the physically adsorbed water on the surface of the catalyst. The catalyst weight loss rate is relatively slow between, 450 and 600 °C, which is mainly due to the decomposition of ammonium tungstate and changing to WO_3 . The thermal weight loss peak at approximately 600 °C is attributed to the formation of tetragonal ZrO_2 phase crystals. The catalyst weight loss rate is low and the weight tends to be constant for temperatures greater than 600 °C. Therefore, the minimum calcination temperature of the catalyst is set as 600 °C.

Figure 7. TG-DTA curves of the Pt/WZ precursor catalyst.

It is observed from Figure 8 that the intensity of the characteristic peak of WO_3 gradually increases as the calcination temperature increases. There is a strong characteristic peak of tetragonal ZrO_2 , and no monoclinic ZrO_2 phase and WO_3 crystals are detected when the calcination temperature is lower than 600–700 °C. This indicates that WO_3 has good dispersibility on the surface of the catalyst at the calcination temperature range. The highly dispersed WO_3 may effectively inhibit the transformation of the metastable tetragonal ZrO_2 . It could also be that the tetragonal ZrO_2 phase is more stable and does not convert to a monoclinic phase at low temperature. The monoclinic ZrO_2 does not show isomerization catalytic activity so that the Cr-Pt/WZ catalyst has the preferred n-heptane isomerization catalytic structure. The monoclinic ZrO_2 and WO_3 crystals begin to form at the calcination temperature of 800 °C. Sharp WO_3 and monoclinic ZrO_2 characteristic peaks appear in the catalyst prepared at the calcination temperature of 900 °C. The catalyst pores collapse, the active components on the surface of the catalyst appears to be sintered, and the crystallinity is higher under a high calcination temperature, which leads to the decrease of the catalyst activity in the n-heptane isomerization reaction.

Figure 8. XRD patterns of the Cr-Pt/WZ catalyst calcined at 600–800 °C.

The specific surface area and pore size and volume of Cr-Pt/WZ catalysts, prepared at different calcination temperatures, are shown in Table 3. It is shown that the specific surface area of the catalyst is gradually reduced from 129.8 to 73.2 m²·g^{−1} when the calcination temperature is increased from 600 °C to 800 °C. Meanwhile, the pore volume is gradually reduced, and the pore size decreases and then increases. It is observed that WO₃ crystals increasingly form on the catalyst surface at first with the increase of the calcination temperature so that the catalyst pores and the pore diameter decrease. Sharp characteristic peaks of WO₃ and monoclinic ZrO₂ appear, and the catalyst pores collapse at the calcination temperature of 900 °C. As a result, the specific surface area, pore volume, and pore diameter of the catalyst decrease sharply, and the active sites and acidic sites in the catalyst decrease so that the catalytic activity decreases.

Table 3. Surface area and pore size and volume of the Cr-Pt/WZ catalysts calcined at 600–800 °C.

Calcination Temperature/(°C)	$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$	$V_{\text{P}}/(\text{cm}^3 \cdot \text{g}^{-1})$	$d_{\text{P}}/(\text{nm})$
600	129.8	0.246	5.81
700	107.9	0.189	6.20
800	103.5	0.177	6.85
900	73.2	0.120	5.20

The NH₃-TPD curves of the Cr-Pt/WZ catalyst calcined at 600–800 °C are shown in Figure 9. It is observed from the figure that the area of the NH₃ desorption peak increases at first and then decreases with the increase of the calcination temperature. This indicates that the total number of acid sites on the catalyst increases at first and then decreases. It is also observed from the figure and table that WO₃ has good dispersibility on the surface of the catalyst and the Cr-Pt/WZ catalyst has a large specific surface area, resulting in a greater number of acidic sites. The catalyst has a strong acidic structure and good catalytic activity at a lower reaction temperature for the calcination temperature of 800 °C. However, the structure of the catalyst changes strongly, and the acidity is weakened when the calcination temperature of the catalyst is too high.

Figure 9. The NH_3 -TPD curves of Cr-Pt/WZ catalyst calcined at 600–800 °C.

2.3.2. Catalytic Activity of the Catalysts

The activity of Cr-Pt/WZ catalysts calcined at 600–800 °C is shown in Figure 10. It is observed that when the reaction temperature is 220 °C and the calcination temperature increases from 600 °C to 800 °C, the conversion of n-heptane increases from 13.3% to 81.5%. However, the heptane conversion rate drops sharply to 3.2% when the calcination temperature is increased to 900 °C. The yield of isomeric heptane has the same trend as the conversion of n-heptane. The yield increases from 13.3% to 73.7% in the range of 600 to 800 °C and then decreases sharply at 900 °C. According to catalyst characterization results, the catalyst pore size gradually increased with the increase in the calcination temperature. The isomeric heptane intermediate product is more easily diffused in the larger channel so that the catalyst activity gradually increases. The characteristic peak of the tetragonal ZrO_2 has a high intensity at the calcination temperature of 600–700 °C. However, Pt loses some metallicity on the tetragonal ZrO_2 phase and maintains high metallicity on the monoclinic phase [24]. Therefore, the activity of the Cr-Pt/WZ catalyst calcined at 600–700 °C is lower than the activity of the catalyst calcined at 800 °C.

Figure 10. Activities of the Cr-Pt/WZ catalysts calcined at 600–800 °C. Reaction condition: $n(\text{H}_2):n(\text{C}_7) = 5 \text{ mol L/mol}$, LHSV = 0.7 h^{-1} , and $P = 1.0 \text{ MPa}$, $T = 200\text{--}300 \text{ }^\circ\text{C}$.

2.4. Catalyst Stability Study

The stability of the catalyst is crucial for the life of the catalyst. As is shown in Figure 11, the stability of Cr-Pt/WZ catalysts with the Cr content of 1.4 wt% and the Pt/WZ catalysts were studied in n-heptane isomerization at the reaction temperature of 220 °C, pressure of 1.0 MPa, ratio of $n(\text{H}_2):n(\text{C}_7) = 9 \text{ mol/mol}$, and $\text{LHSV} = 1.0 \text{ h}^{-1}$. The conversion rate of n-heptane and the yield of heterogeneous heptane are relatively stable. Compared to the Pt/WZ catalyst, the conversion of n-heptane and the yield of heterogeneous heptane over the Cr-Pt/WZ catalyst are significantly higher. Moreover, the Pt/WZ catalyst was deactivated after the reaction was carried out for 300 h. However, the Cr-Pt/WZ catalyst shows good stability and is a promising approach for industrial application.

Figure 11. Study on stability of Cr-Pt/WZ catalyst.

It can be seen from SEM images of the catalyst before and after reaction (shown in Figure 12) that the particles on the surface of the catalyst are more uniformly dispersed before the reaction, and some particles of the catalyst are aggregated after the reaction. The agglomeration of catalyst causes a decrease of the catalyst activity and the catalyst is gradually deactivated with time.

Figure 12. SEM of the Cr-Pt-WZ catalyst before and after the reaction. Magnification of the electron microscope: 10,000.

2.5. Application of Catalyst in the Industrial Raw Material Isomerization

To study the activity of the Cr-Pt/WZ catalyst over industrial raw materials, the isomerization reaction was carried out using lighter naphtha fractions above 75 °C under the condition of 220 °C, 1.0 MPa, $n(\text{H}_2):n(\text{C}_7) = 9 \text{ mol/mol}$, and $\text{LHSV} = 1.0 \text{ h}^{-1}$. Tables 4–6 show the PIONA (paraffins, isoparaffins, olefins, naphthenes, aromatics, and oxygenates) composition of the lighter naphtha raw material, and the reaction products after 48 h and 100 h operation, respectively. It is observed that the straight chain alkanes are heterogeneous products of cyclanes, aromatics, or a smaller number of carbon atoms when the Cr-Pt/WZ catalyst is used. The chromatographic octane number of the product increased from the initial 30.6 to 58.9 after 48 h operation and 57.6 after 100 h operation, respectively. It can also be seen from the table that the isomerization works better for C7 and smaller moleculars. It is recommended to separate C5 to C7 from the raw materials and then feed it into the isomerize process. The contents of n-C5, i-C5, n-C6, and i-C6 in the products increase, indicating that bigger molecules such as C8, C9, and C10, are relatively easy to crack. The appearance of C3 and C4 indicates that cracking occurs to a certain degree during the isomerization process. The C3 and C4 content changes in the products indicates that the cracking activity decreases and the isomerization activity also decreases slightly as the reaction progresses. After 100 h of the light naphtha feedstock reaction, the catalyst was not deactivated, and the combined catalyst was not deactivated after 500 h of n-heptane isomerization reaction, indicating that the catalyst has good stability.

Table 4. The PIONA composition of the light naphtha raw material above 75 °C.

CNum	N-P	I-P	O	N	A	Total
C-5	0.25	0.18	0.00	0.36	0.00	0.79
C-6	4.55	4.04	0.04	2.82	0.02	11.47
C-7	9.92	14.40	0.62	1.33	0.11	26.38
C-8	11.39	16.87	0.00	2.46	0.61	31.33
C-9	8.95	8.51	0.00	3.25	0.10	20.81
C-10	1.84	5.16	0.00	0.36	0.08	7.44
C-11	0.26	1.34	0.00	0.00	0.00	1.60

Table 5. The product of light naphtha Isomerization (48 h).

CNum	N-P	I-P	O	N	A	Total
C-3	0.37	0.00	0.00	0.00	0.00	0.37
C-4	1.55	6.72	0.00	0.00	0.00	8.27
C-5	2.11	10.93	0.00	0.00	0.00	13.04
C-6	6.04	14.36	0.00	1.55	0.00	21.95
C-7	7.14	32.84	0.00	3.19	0.01	43.18
C-8	1.32	6.21	0.00	3.21	0.08	10.82
C-9	0.32	0.79	0.00	1.18	0.00	2.29
C-10	0.03	0.08	0.00	0.00	0.00	0.11

Table 6. The product of light naphtha Isomerization (100 h).

CNum	N-P	I-P	O	N	A	Total
C-3	0.22	0.00	0.00	0.00	0.00	0.22
C-4	1.16	4.76	0.00	0.00	0.00	5.92
C-5	1.91	9.96	0.00	2.01	0.00	13.88
C-6	6.58	12.96	0.00	1.70	0.00	21.24
C-7	8.05	32.79	0.00	3.91	0.01	44.76
C-8	1.35	6.46	0.00	3.54	0.09	11.44
C-9	0.26	0.89	0.00	1.30	0.00	2.45
C-10	0.02	0.06	0.00	0.00	0.00	0.08

3. Experimental

3.1. Catalyst Preparation

The mixed hydroxide $\text{Cr}(\text{OH})_3\text{-Zr}(\text{OH})_4$ was prepared from ZrOCl_2 -containing $\text{Cr}(\text{NO}_3)_3$ solution by dropwise addition of an ammonia water solution under vigorous stirring up to pH 9~10. The precipitated hydrogel was aged at room temperature for 24 h and refluxed at 100 °C for 24 h. Then, it was filtered and washed with deionized water repeatedly until no chloride ions were detected. The gel was dried at 80 °C overnight. $\text{Cr}_2\text{O}_3/\text{WO}_3/\text{ZrO}_2$ was obtained by impregnation of aqueous ammonium tungstate, drying at 80 °C overnight, and calcining at 800 °C in static air for 3 h. $\text{Pt}/\text{Cr}_2\text{O}_3/\text{WO}_3/\text{ZrO}_2$ was prepared by $\text{Cr}_2\text{O}_3/\text{WO}_3/\text{ZrO}_2$ infiltration with an H_2PtCl_6 solution with 0.35 wt% Pt content in the catalyst followed by drying at 80 °C overnight and calcining at 450 °C in static air for 3 h. The $\text{Pt}/\text{WO}_3/\text{ZrO}_2$ catalyst was prepared by the same method mentioned above. The catalysts prepared were designated as Cr-Pt/WZ and Pt/WZ, respectively.

3.2. Catalyst Characterization

X-ray diffraction (XRD) patterns of the catalysts were obtained using an XRD-7000 instrument (Shimadzu, Tokyo, Japan) with Cu-K α radiation at 40 kV and 30 mA and $2\theta = 20\text{--}70^\circ$, with steps of $4^\circ/\text{min}$. The Brunner–Emmet–Teller measurements (BET) surface area and pore volume of the catalysts were obtained using an Autosorb-1 instrument (Quantachrome, FL, USA) using N_2 as the adsorbent. The thermogravimetry-differential heat (TG-DSC) analysis for the samples was carried out using an SDT-Q600 thermal analyzer made by the American TA Company, (New Castle, KY, USA). The air was used as the carrier gas, the flow rate was $100\text{ mL}\cdot\text{min}^{-1}$, and the temperature range was 50~860 °C. The temperature increasing rate was $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$. Detailed hydrocarbon analysis (DHA) of petroleum samples was obtained by an Agilent 7890 GC/FID (Santa Clara, CA, US) equipped with an Agilent 7683B Automatic Liquid Sampler, (Santa Clara, CA, USA), pre-fractionating inlet, ultra-high resolution column, flame ionization detector, and a data acquisition system. These testing methods are also referred to as PIONA because they can be used to characterize components by their hydrocarbon compound class (paraffins, isoparaffins, olefins, naphthenes, aromatics, and oxygenates).

The acidity of the catalyst was analyzed by NH_3 -programmed desorption using Micromeritics Autochem HP2920 (Atlanta, GA, USA) automatic multi-function temperature-programming analyzer. The samples were heated in a helium flow with 10% vol O_2 up to 700 °C and were kept at that temperature for one h. Then, the samples were cooled in flowing helium at 100 °C and ammonia adsorption was carried out for one h using a mixture gas of 10% vol. NH_3 and 90% vol. helium. Weakly bounded ammonia was removed by blowing-off using helium gas at a temperature of 100 °C for one h. The temperature was then raised to 700 °C at a rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ in a helium gas flow, and desorption was recorded to obtain a NH_3 -TPD curve.

3.3. Catalytic Tests and Product Analysis

3.3.1. Catalytic Tests

The diagram of n-heptane isomerization reaction devices is shown in Figure 13. The isomerization of n-heptane was performed in a fixed-bed flow reactor at a pressure of 1.0 MPa and a temperature of 200–260 °C. Before starting the reaction, the catalyst was pretreated in flowing air at 450 °C for three h and then reduced in flowing hydrogen at 250 °C for two h. Then, the reactor was cooled to the reaction temperature and n-heptane was fed at a liquid hourly space velocity (LHSV) of 0.7 h^{-1} and an $\text{H}_2/\text{n-heptane}$ ratio of nine (mol/mol).

Figure 13. PID (Piping & Instrument Diagram) diagram of the experimental device of n-heptane isomerization. 1 feedstock tank, 2 feed pump, 3 pressure reducing valve, 4 mass flowmeter, 5 check valve, 6 reactor, 7 loop condenser, 8 products tank, and 9 back pressure valve.

3.3.2. Product Analysis

The reaction products were qualitatively analyzed by gas chromatography-mass spectrometry (6890/5973N, Agilent Technologies, Santa Clara, CA, USA). A gas chromatograph (GC-14C, Shimadzu Corporation, Tokyo, Japan) was used and the n-heptane conversion and its isomer yield in the experiment were analyzed. The catalyst evaluation is based on the conversion of n-heptane and the total yield of isomeric heptane (referred to as iC_7) as the catalyst activity evaluation standard. The specific calculation method is as follows:

N-heptane conversion rate:

$$X = \frac{\omega(nC_7)_{Reactants} - \omega(nC_7)_{Products}}{\omega(nC_7)_{Reactant}} \times 100\% \quad (1)$$

Total selectivity of isomeric heptane:

$$S = \frac{\sum \omega(iC_7)}{\sum \omega(iC_7) + \omega(C_1 - C_6)} \times 100\% \quad (2)$$

Total yield of isomeric heptane:

$$Y = X \times S \times 100\% \quad (3)$$

The $\omega(nC_7)_{Reactants}$ and $\omega(nC_7)_{Products}$ in the formula are the raw materials and the n-heptane mass fraction in the product, and $\omega(iC_7)$ and $\omega(nC_1 - C_6)$ are the mass fractions of the isomeric heptane and $C_1 - C_6$ cleavage products in the product.

4. Conclusions

Different amounts of the Cr transition metal were loaded to the Pt/WZ catalyst. The Pt/ WO_3 / ZrO_2 catalyst with 1.4 wt% Cr loading shows stronger characteristic peaks of the tetragonal ZrO_2 phase, stronger acidity, and larger specific surface area and demonstrates better catalytic performance in n-heptane isomerization. The WO_3 loading strongly affects the activity of the catalyst. The optimal catalyst activity was obtained at the WO_3 loading of 18 wt%. The calcination temperature has an influence on the structure of the catalyst, and in turn, affects the activity of the catalyst. When the catalyst is calcined at 800 °C, WO_3 has good dispersibility over the surface of the catalyst; meanwhile,

WO₃ and ZrO₂ form a relatively stable acidic structure, and the catalyst has better activity at lower reaction temperatures. The conversion of n-heptane reached 81.5%, and the isomeric heptane yield reached 73.7% over Cr-Pt/WO₃/ZrO₂ catalyst under the conditions of 220 °C, 1.0 MPa, n(H₂):n(C₇) = 9 mol/mol, and LHSV = 1.0 h⁻¹. The catalyst shows no deactivation in the n-heptane isomerization for 500 h and shows better stability than Pt/WO₃/ZrO₂. At the same time, Cr-Pt/WO₃/ZrO₂ catalysts have good isomerization performance in industrial naphtha raw materials, and the chromatographic octane number increases by approximately 28 units through the isomerization process.

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