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Isomerization of *n*-pentane over platinum promoted tungstated zirconia supported on mesoporous SBA-15 prepared by supercritical impregnation

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Abstract

Tungstated zirconia was supported on mesoporous SBA-15 by impregnation in supercritical ethanol. The resultant catalyst promoted with 1 wt% of Pt shows 100% selectivity of iso-pentane and two times higher conversion in n-pentane isomerization than the one prepared by conventional impregnation. Supercritical impregnation exerts no destruction of the porous silica and offers better dispersion of tungstated zirconia than conventional impregnation. Optimized loading of WO₃/ZrO₂/SBA-15 is 20/40/40 wt%, which infers to 2.4 W-atoms/ nm² and 8.9 Zr-atoms/nm² dispersed on the SBA-15 support. Moreover, introducing a proper mole fraction of hydrogen in the reactants markedly improves the catalytic activity in *n*-pentane isomerization. The role of hydrogen was not only served as the reactants, it also acted to regenerate Brønsted acid sites during *n*-pentane isomerization. However, overdose of hydrogen leaded to a leveling-off in the rate of isomerization and enhanced hydrogenolysis reaction. The in situ IR spectroscopic studies suggested that Brønsted acid sites were the active centers for the isomerization. A reaction mechanism was, therefore, proposed that heterolytic fission of hydrogen and dehydrogenation of *n*-pentane took place over Pt. The secondary carbocation formed over Brønsted acid sites was rearranged to a tertiary carbocation by methyl migration, followed by reacting with a hydride to generate iso-pentane.

KEYWORDS

acid catalyst, n-pentane isomerization, Pt, SBA-15, supercritical fluid, tungstated zirconia

1 | INTRODUCTION

Strong mineral acids, such as HF and H₂SO₄, are commonly used in current petrochemical industries. Such catalytic processes generate a large amount of nonrecyclable acid wastes, which are hazardous to the environment. Great efforts have been made in seeking the alternative acids, especially the solid acids, in order to replace the strong mineral acids.^[1] Solid acid catalysts have been used in modern refiners in isomerization process to produce high-octane gasoline components from low-octane light naphtha fractions. However, coke formation and retention of heavy side products on solid catalysts in the pores are the most frequent causes of catalyst deactivation in industrial processes.^[2]

Sulfated zirconia and tungstated zirconia have been studied as strong solid acid catalysts because they show high catalytic activities in skeletal isomerization of alkanes at relatively low temperatures.^[2,3] Arata and Hino classified the sulfated and tungstated zirconia materials to be superacid catalysts.^[4,5] However, acidity measurements have shown that their acid strengths are merely in medium to strong range.^[6] The catalytic activities decayed markedly with time-on-stream as the active acid sites were covered by coke during alkane isomerization. Moreover, the loss of sulfur species during the catalytic reactions also contributed to the deactivation of sulfated zirconia catalysts. As to tungstated zirconia, the low surface areas (around 50 m²/g) may also contribute to the fast deactivation.

Mesoporous siliceous materials, which contain high surface areas (600–1,000 m^2/g) and tunable ordered large pores (2-10 nm) have been considered to be potential supports to increase the dispersion of solid acid catalysts.^[6-9] Sulfated zirconia supported on siliceous Mobil Composition of Matter No. 41 (MCM-41) has been reported to enhance the catalytic activities in *n*-butane isomerization.^[7-9] Mixed tungstate-zirconia has been supported on various porous silica materials, such as Santa Barbara Amorphous-15 (SBA-15), MCM-41 and silica gel,^[6] and their catalytic activities in n-pentane isomerization were compared. SBA-15 supported tungstate-zirconia has shown better conversion and iso-pentane selectivity than MCM-41 support, attributing to that SBA-15 could maintain the ordered porous structure after loading with W/Zr mixed oxides whereas MCM-41 and silica gel could not.

Supercritical (SC) fluids own characteristics of low viscosity, high diffusivity, and extremely low surface tension, which reduce the mass transfer restriction of the dissolved solutes.^[10] Several research groups have applied SC media to synthesize small crystalline metal oxides by thermal decomposition of the metal precursors dissolved in SC fluids. Chhor and his coworkers^[11] investigated the synthesis of submicron TiO₂ powders by thermal decomposition of the metal alkoxide in a SC ethanol at 350°C. The as-prepared TiO_2 particles in 30–60 nm were well crystallized in anatase phase, and no further thermal treatment was needed. Hayashi et al.^[12] prepared titania nanoparticles (20-115 nm) with mesoporosity (4-25 nm) by hydrothermal treatment under various subcritical and SC water conditions. The pore size and crystallinity of TiO₂ can be tuned by changing the hydrothermal temperature between 100 and 400°C. Morère et al.^[13] reported the deposition of Pd onto SBA-15 silica using SC CO₂ at a mild condition of 40°C and 85 bar. Nano-sized Pt particles (6-9 nm) were found to uniformly disperse over SBA-15.

In the present study, tungstated zirconia (WZ) catalysts supported on mesoporous SBA-15 were prepared by conventional and SC impregnation. SC ethanol is considered a proper solvent to use because it is a polar solvent and the critical temperature at 241°C is much lower than that of water (373°C). The acidities of the resultant materials were characterized by ammonia temperatureprogrammed desorption (TPD) and pyridine sorption, Isomerization of *n*-pentane was studied to evaluate the catalytic performance of the prepared samples. Several factors were examined to obtain the optimization condition of the catalytic system—the weight ratios of WO₃, ZrO_2 , and SBA-15, the introduction of hydrogen into the reactants, and the promotion effect of Pt. Moreover, a reaction mechanism of *n*-pentane isomerization over the Pt-promoted WZ catalysts was proposed.

2 | RESULTS AND DISCUSSION

2.1 | Characterization of WO₃-ZrO₂/SBA-15 catalysts

Figure 1 shows the X-ray diffraction (XRD) patterns of Pt-promoted WZ supported on SBA-15 prepared by conventional and SC impregnation. A WZ sample without SBA-15 support (named WZ(SC)) is also shown as a reference catalyst. The triplet diffraction peaks at $2\theta = 23.1^{\circ}$, 23.6°, and 24.4° and duplet peaks at $2\theta = 34.8^{\circ}$ and 35.1° are the characteristic peaks of monoclinic WO₃,^[14] while the strong diffraction at 30.5° corresponds to tetrahedral ZrO₂ phase. For tungsten oxide deposited sample, Pt/W (SC)/SBA-15, only WO₃ phase was observed accordingly. For SBA-15 supported WZ prepared by conventional impregnation, Pt/WZ(IM)/SBA-15 shows stronger diffraction peaks of WO₃ than Pt/WZ(SC)/SBA-15, indicating that smaller particle size of WO₃ is formed by SC impregnation. Moreover, tungsten oxide deposited sample Pt/W (SC)/SBA-15 has more intense diffraction peaks of WO₃



FIGURE 1 XRD patterns of SBA-15 and various $Pt/WO_3/ZrO_2$ loading samples. For Pt/WZ/SBABA-15 materials, $Pt/WO_3/ZrO_2$ loadings = 1/20/40 wt%. For WZ(SC), $WO_3/ZrO_2 = 20$ wt%

than WZ deposited sample Pt/WZ(SC)/SBA-15. It implies that ZrO_2 may improve the dispersion of WO_3 during catalyst preparation.

In the small angle diffraction region, three distinct diffraction peaks corresponding to (100), (110), (200) planes of 2D-hexagonal *p6mm* symmetry are visible for pure SBA-15.^[15] After the deposition of either tungsten oxide or WZ onto SBA-15, remarkable decreases in (100) peak are observed, and the (110) and (200) diffraction peaks almost disappear. Such results are due to the decrease in the diffraction contrast or the ordered hexagonal channels of SBA-15 being disturbed after filling the volume of mesoporous channels with oxides. Moreover, the (100) signal of Pt/WZ(IM)/SBA-15 shifts slightly toward high angle and is more pronounced in lowering the intensity than that of Pt/WZ(SC)/SBA-15.

Table 1 summarizes the surface area and pore volume of the aforementioned samples. Pure SBA-15 shows a surface area of 698 m²/g and pore volume of 0.79 cm³/g. A much lower Brunauer–Emmett–Teller (BET) surface area and pore volume of Pt/WZ(IM)/SBA-15 (33 m²/g and 0.04 cm³/g) than SBA-15 demonstrate that the pore channels have been blocked by or filled with WZ during conventional impregnation. On the other hand, loading WZ

by SC impregnation shows a less decrease in surface area and pore volume (219 m²/g and 0.50 cm³/g) albeit still lower compared with pure SBA-15. It suggests a better dispersion of WZ on SBA-15 by SC than conventional impregnation. That is also evidenced by the smaller crystallite size of ZrO_2 (11.2 vs. 7.4 nm) as shown in Table 1. To confirm the influence of SC condition on the pore structure of SBA-15, a control, SBA-15(SC), was conducted by treating SBA-15 in SC ethanol at 270°C for 3 hr. A mild decrease in BET surface area and pore volume was obtained. The corresponding XRD pattern, N₂ physisorption isotherm and pore size distribution are shown Figures S2 and S3, which displays only small changes in the pore structure after treating SBA-15 in SC ethanol.

2.2 | Catalytic evaluation

Isomerization of *n*-pentane is performed at 250° C for 20 hr, and the products were analyzed every 30 min. Figure 2 shows the time-on-stream catalytic performances of various samples in *n*-pentane isomerization. Higher conversions of *n*-pentane were observed in the

| Sample | W/Z^a | Z/SBA ^a | $d_{ m ZrO2}(m nm)^{b}$ | $S_{\rm BET}~({ m m^2/g})$ | $V_{\rm p}~({\rm cm}^3/{\rm g})$ | Conv. (%) ^c | Select. (%) ^c | Yield (%) ^c |
|-------------------------|---------|--------------------|--------------------------|----------------------------|----------------------------------|------------------------|--------------------------|------------------------|
| SBA-15 | - | - | - | 698 | 0.79 | n.d. | n.d. | n.d. |
| SBA-15(SC) ^d | - | - | - | 613 | 0.78 | n.d. | n.d. | n.d. |
| Pt/HY | - | - | - | 565 | 0.39 | 54 | 98 | 53 |
| WZ(SC) | 0.2 | - | | 46 | 0.19 | 44 | 100 | 44 |
| W(SC)/SBA-15 | - | - | - | 189 | 0.38 | 1 | 100 | 1 |
| Pt/WZ(IM)/SBA-15 | 0.5 | 1.0 | 11.2 | 33 | 0.04 | 25 | 97 | 24 |
| Pt/WZ(SC)/SBA-15 | 0.3 | 0.3 | n.d. ^e | 480 | 0.70 | 6 | 73 | 4 |
| | 0.5 | 0.3 | n.d. | 397 | 0.60 | 15 | 100 | 15 |
| | 0.1 | 0.5 | n.d. | 431 | 0.61 | 2 | 62 | 1 |
| | 0.3 | 0.5 | n.d. | 358 | 0.57 | 36 | 99 | 36 |
| | 0.5 | 0.5 | 5.9 | 331 | 0.61 | 48 | 100 | 48 |
| | 0.3 | 1.0 | 7.9 | 237 | 0.46 | 37 | 99 | 37 |
| | 0.4 | 1.0 | 7.4 | 216 | 0.42 | 44 | 99. | 44 |
| | 0.5 | 1.0 | 7.4 | 219 | 0.50 | 66 | 99 | 65 |
| | 0.6 | 1.0 | 7.5 | 167 | 0.39 | 48 | 99 | 48 |
| | 0.7 | 1.0 | 8.1 | 164 | 0.38 | 49 | 99 | 49 |
| | 0.5 | 1.5 | 9.8 | 154 | 0.40 | 36 | 99 | 36 |

TABLE 1 Physical properties and catalytic activities in *n*-pentane isomerization of porous silica, oxides, and Pt-promoted catalysts

^aW/Z and Z/SBA stand for the weight ratios of WO₃ to ZrO₂, and ZrO₂ to SBA-15.

^bThe crystalline size of ZrO_2 was calculated by Scherrer's equation on the XRD peak 2θ at 30.5° .

^cThe conversions and selectivities were obtained at 10 hr on feed. Reaction condition: 250°C, H₂: N₂: n-pentane = 2: 10: 0.37 (ml/min).

WHSV = $1,484.4 \text{ ml/g}_{cat}$ -h.

^dSBA-15 was treated in supercritical ethanol at 270°C for 3 hr.

en.d., not-determined.



FIGURE 2 Time on stream profiles of catalytic activities in *n*-pentane isomerization over various catalysts: Pt/WZ(SC) (\blacksquare), Pt/WZ(IM)/SBA-15s (\bullet), Pt/WZ(SC)/SBA-15 (\blacktriangle), Pt/W(SC)/SBA-15 (\blacktriangledown), and Pt-HY (\bullet). Pt/WO₃/ZrO₂ loadings = 1/20/40 wt%. Reaction condition: 250°C, H₂: N₂: *n*-pentane = 2:10: 0.37 (ml/min). WHSV = 1,484.4 ml/g_{cat}-h

initial stage (less than 1 hr) and the conversion decreases with time-on-stream gradually for all the tested samples. In contrast, iso-pentane selectivities were lower in the initial stage and then increased to and retained above 95% after 1 hr on stream. The conversions of *n*-pentane as well as the selectivities and yields of iso-pentane at 10 hr of reaction are summarized in Table 1. W/Z and Z/SBA represent the weight ratios of WO₃/ZrO₂ and ZrO₂/SBA-15, respectively. It is noticeable that the yields of iso-pentane are close to the *n*-pentane conversions since most of the iso-pentane selectivities are close to 100%. Over the unsupported Pt/WZ(SC) catalyst, 40% conversion of npentane and nearly 100% selectivity of iso-pentane were obtained. However, only half of the conversion (25%) and slightly lower selectivity (97%) was reached over Pt/WZ (IM)/SBA-15 (W/Z = 0.5, Z/SBA = 1). These results indicate that loading WZ on SBA-15 by conventional impregnation failed to promote the catalytic activity. In contrast, the counterpart prepared by SC impregnation, Pt/WZ(SC)/ SBA-15 (W/Z = 0.5, Z/SBA = 1) gave 66% conversion of *n*-pentane and 99% selectivity of *iso*-pentane. The catalytic activity is markedly improved in comparison with that of unsupported Pt/WZ(SC).

Pentane isomerization is a thermodynamic equilibrium reaction. At reaction temperature of 250°C, the equilibrium *iso*-pentane composition in pentane isomers is about 70%.^[16] Accordingly, 70% conversion of *n*-pentane and 100% selectivity of *iso*-pentane would be the optimal values to achieve. The catalytic result obtained over Pt/WZ(SC)/SBA-15 (**W**/**Z** = 0.5, **Z**/**SBA** = 1) is close to this optimal values.

SBA-15 supported tungsten oxide, Pt/W(SC)/SBA-15, was also tested to study the role of zirconia in *n*-pentane



FIGURE 3 Catalytic activities of the Pt/WZ(SC)/SBA-15 catalysts with different weight ratios of WO₃/ZrO₂ and ZrO₂/SBA-15 in *n*-pentane isomerization. Reaction condition: reaction temperature = 250°C, H₂: N₂: *n*-pentane = 2:10: 0.37 (ml/min). WHSV = 1,484.4 ml/g_{cat}-h

isomerization. Less than 1% conversion of *n*-pentane was achieved albeit 100% selectivity of *iso*-pentane was obtained, inferring that zirconia is an essential ingredient in the mixed oxide catalyst. On the other hand, Pt-promoted H^+ -form Y-typed zeolite prepared by conventional impregnation (Pt/HY) was found to give rather high *n*-pentane conversion (54%) and *iso*-pentane selectivity (98%). However, the activity of Pt/HY is still lower than that of Pt/WZ(SC)/SBA-15.

2.3 | Optimization of WO₃/ZrO₂ loading

Since SC impregnation is efficient in preparing SBA-15 supported WZ catalysts with high activities in *n*-pentane isomerization, an extensive study on the effects of WO₃ and ZrO₂ loadings on Pt/WZ(SC)/SBA-15 catalysts is carried out and the results are listed in Table 1. Both $WO_3/$ ZrO_2 (W/Z) and ZrO_2 /SBA-15 (Z/SBA) weight ratios show impacts on catalytic activities. Relatively low npentane conversions were obtained over the catalysts with the W/Z < 0.3 and Z/SBA < 0.5. The *n*-pentane conversion increases with the increases in WO₃ and ZrO₂ loadings, and an optimal *n*-pentane conversion of 66% with iso-pentane selectivity of 99% was obtained over the catalyst with W/Z = 0.5 and Z/SBA = 1. However, further increases in WO₃ and ZrO_2 loadings would lower *n*pentane conversion, probably due to the accompanying blockage of pores and decrease in surface area.

The conversion-selectivity plots shown in Figure 3 demonstrate that high *iso*-pentane selectivities (nearly 100%) are achieved when the samples have relatively high loadings of both WO₃ and ZrO_2 . That is both **W/Z**

and **Z/SBA** ratios need to be larger than 0.3. On the other hand, high ZrO_2 loadings enhance the *n*-pentane conversion, and the maximum conversion is obtained at **Z**/ **SBA** = 1. When fixing the **Z/SBA** ratio at 1, there is an optimal loading of **W**O₃. The conversion increases from 36 to 67% as the **W/Z** ratio is increased from 0.3 to 0.5, but it decreases to 49% as **W/Z** is further increased to 0.7.

Figure 4 shows the XRD patterns of the series of catalysts with the **Z/SBA** ratios fixed at 1 and the **W/Z** ratios varied from 0.3 to 0.7. Triplet diffraction peaks between $2\theta = 22^{\circ}$ and 25° of monoclinic WO₃ are observed when the **W/Z** ratio is higher than 0.5. In the small angle region of Figure 4, the intensity of the (100), (110), and (200) diffraction peaks of SBA-15 decreases with the WO₃ loading. Moreover, BET surface areas and pore volumes of these samples decrease with WO₃ loading (Table 1). These results imply that the WO₃ crystallites should fill in the pores of SBA-15 and the size of the WO₃ crystallites increases with WO₃ loading.

Figure 5 shows the XRD patterns of the series of the catalysts with the **W/Z** ratio fixed at 0.5 and the **Z/SBA** ratio varied from 0.5 to 1.5. With the increase in ZrO_2 loading, the diffraction peak of tetrahedral ZrO_2 at $2\theta = 30.5^{\circ}$ becomes sharper and more intense, inferring the increase in size and crystallinity of ZrO_2 . Again, the deposition of WZ inside the pore channels of SBA-15 is evidenced by the diminishing of diffraction peaks of SBA-15 in small angle region as the **Z/SBA** ratio increases. Apart from the ZrO_2 crystallites, diffraction peaks of monoclinic WO₃ become predominant on the catalyst with the highest **Z/SBA** ratio of 1.5. Table 1 also shows that this sample has the lowest BET surface (154 m²/g) and pore volume (0.4 cm³/g) among the three shown in



FIGURE 4 XRD patterns of Pt/WZ(SC)/SBA-15 catalysts with WO_3/ZrO_2 weight ratios varied in (1) 0.7, (2) 0.6, (3) 0.5, (4) 0.4, (5) 0.3. The ZrO_2/SBA-15 weight ratio is 1.0 for all the samples

Figure 5. In comparison of their catalytic activities in *n*-pentane isomerization, the one with $\mathbf{Z}/\mathbf{SBA} = 1$ has the highest *n*-pentane conversion of 66% while the one with $\mathbf{Z}/\mathbf{SBA} = 1.5$ has the lowest conversion of 36%. The poor catalytic activity of the latter sample may be attributed to the formation of large WO₃ and ZrO₂ crystallites, which not only reduce the active surface area of WO₃ but also block the channeling pores of SBA-15.

Figure 6 depicts the *n*-pentane conversion over Pt/WZ(SC)/SBA-15 with different surface concentrations of WO₃ and ZrO₂. The surface concentrations were



FIGURE 5 XRD patterns of Pt/WZ(SC)/SBA-15 catalysts with $ZrO_2/SBA-15$ weight ratios varied in (a) 0.5, (b) 1.0, (c) 1.5. The WO_3/ZrO_2 weight ratio is 0.5 for all the samples



FIGURE 6 Conversions of *n*-pentane over Pt/WZ(SC)/SBA-15 catalysts with different surface WO₃ and ZrO₂ concentrations. Reaction condition: 250°C, H₂: N₂: *n*-pentane = 2:10: 0.37 (ml/min). WHSV = 1,484.4 ml/g_{cat}-h

determined by the loading of the component (WO₃ or ZrO₂) and the surface area of the catalyst.^[17] The surface ZrO₂ concentrations were found to vary in a broad range from 2.2 to 14.6 Zr-atoms/nm², and tetrahedral ZrO₂ phase $(2\theta = 30.5^{\circ})$ were observed in the XRD patterns. The *n*-pentane conversion increases with WO₃ concentration and achieves an optimal value when WO₃ concentration is around 2.5 W-atoms/nm². The *n*-pentane conversion drops as WO₃ concentration is higher than 3.5 atoms/nm², and the XRD patterns show monoclinic WO₃ phase ($2\theta = 23.1^{\circ}$, 23.6° , and 24.4°) in these samples. Naito et al.^[18] reported that monolayer of WO₃ on ZrO₂ corresponds to the surface concentration of 3.5-4.0 atoms/nm², and surface WO₃ concentration predominantly influences the conversion of n-pentane. Overdosing WO₃ of more than a monolayer leads to the formation of bulk WO₃ and lowers the catalytic activity of the catalysts. However, among the Pt/WZ(SC)/SBA-15 samples, the highest conversion in *n*-pentane isomerization to *iso*-pentane lies in the one with $WO_3/ZrO_2 = 0.5$ and $ZrO_2/SBA-15 = 1$, corresponding to the surface concentration of 2.4 W-atoms/nm² and 8.9 Zr-atoms/nm². The discrepancy may be caused by different catalytic systems. Herein, we tend to focus on the change in surface concentration, as plotted in Figure 6. The optimized loading of $WO_3/ZrO_2/SBA-15$ is used for the further discussions on the H₂ effect.

2.4 | Effect of hydrogen on catalytic activity and regeneration

Figure 7 shows the time-on-stream catalytic profiles of the Pt/WZ(SC)/SBA-15 catalyst with different partial



FIGURE 7 Effect of hydrogen pressure on the catalytic activities of Pt/WZ(SC)/SBA-15 catalyst in *n*-pentane isomerization. Reaction condition: 250°C, H₂: N₂:*n*-pentane = x: (12 – x): 0.37 (ml/min), where x = 0, 2, 4, 6, or 10. WHSV = 1,484.4 ml/g_{cat}-h

pressures of hydrogen in the stream of *n*-pentane and nitrogen. Nitrogen is used as the inert component to keep the total flow rate of hydrogen and nitrogen at 12 ml/min. In the absence of hydrogen in the gas stream, the catalytic activity of the catalyst decreases dramatically with time-on-stream. The *n*-pentane conversion continuously decreases from 75 to 19% after 10 hr of reaction and the iso-pentane selectivity decreases from 96 to 65% after 18 hr of reaction. Introduction of hydrogen significantly retards the decay of catalytic activity. With 2 ml/min hydrogen, the conversion decreases from 74% at beginning to 66% and selectivity retains ~99.4% after 10 hr on-stream. When H₂ flow-rate is raised to 4 ml/min, the conversion after 10 hr onstream is retained at 70% while the selectivity only decreases slightly to 97%. Further increasing the H₂ flow-rates up to 10 ml/min have little impact on improving the conversion, while the iso-pentane selectivity decreases. Analyzing the products by means of mass spectroscopy, C1-C6 alkanes and branched compounds were found as the byproducts of n-pentane isomerization. Figure 8 shows that more methane, ethane, propane, and butane are formed as byproducts when the hydrogen flow rate increases from 2 to 10 ml/min. According to the literature reports,^[19,20] increasing hydrogen concentration would enhance hydrogenolysis of alkanes. Therefore, the selectivity of iso-pentane decreases with the increase in hydrogen partial pressure.



FIGURE 8 By-product distributions (except for *iso*-pentane) in *n*-pentane isomerization over Pt/WZ(SC)/SBA-15 catalyst in different hydrogen pressures. Reaction condition: 250° C, 5 hr, H₂: N₂:*n*-pentane = *x*: (12 - *x*): 0.37 (ml/min), where *x* = 2, 4, 6, or 10. WHSV = 1,484.4 ml/g_{cat}-h

Khurshid et al.^[21] reported a slightly negative rate of heptane isomerization over Pt/WO₃-ZrO₂ in a high H₂ pressure range (<0.3 MPa) and a positive rate in a low H₂ pressure range (<0.3 MPa). In the present study, 2 ml/min of H₂ in a total flow of 12.37 ml/min corresponds to ~0.016 MPa of H₂ pressure, and 10 ml/min of H₂ corresponds to ~0.08 MPa of H₂ pressure. In other words, our experimental conditions were in low H₂ pressure range (<0.3 MPa) of Khurshid et al. A similar positive effect on *n*-pentane isomerization was found in our study. On the other hand, the report that cracking products were markedly suppressed under a high H₂ pressure is different from what was observed in the present study. According to Figure 8, more cracking products were detected at higher H₂ flow (10 ml/min) than in lower H₂ flow (2 ml/min) condition. Since the selectivity of the target product iso-pentane was much more pronounced than the cracking byproducts, further investigations of the influence of H₂ partial pressure on the cracking reaction was not carried out.

Coke deposition during the isomerization reaction is the inherent problem for the catalyst deactivation. Many studies have reported the coke formation during *n*-alkane isomerization over solid acid catalysts.^[22-25] Figure S4 shows the thermal gravimetric analyses and the differential profiles of the fresh and used Pt/WZ (SC)/SBA-15 catalysts. There is a distinguishable weight loss between 350 and 450°C, attributing to the burned coke. In order to investigate the deactivation and regeneration behavior of the catalyst, the used Pt/WZ(SC)/SBA-15 catalyst was heated in air at 450°C for 6 hr to regenerate. The results of the recycling experiments for three times are shown in Figure 9, and



FIGURE 9 Reusability of Pt/WZ(SC)/SBA-15 catalyst in *n*pentane isomerization. Reaction condition: 250°C, H₂: N₂: *n*pentane = 4:8: 0.37 (ml/min). WHSV = 1,484.4 ml/g_{cat}-h. The used catalyst was regenerated by heating under flowing air at 450°C for 6 hr

the *n*-pentane conversion and *iso*-pentane selectivity are well resumed after regeneration.

2.5 | Surface acid sites of the Pt/WZ/ SBABA-15 catalysts

TPD of adsorbed ammonia is used to characterize the amount of acid sites over the catalysts.^[6,26] Figure S5 compares the profiles of desorbed NH₃ over SBA-15 supported or unsupported WZ by recording the NH₂⁺ (m/z = 16) signals during desorption. All the catalysts show similar TPD-Mass profiles of a wild desorption between 150 and 500°C, mainly corresponding to the weak acid sites. As observed in Figure S5, the SBA-15 supported WZ catalysts display larger peak areas than that of the unsupported one. Furthermore, the supported WZ catalyst prepared by conventional impregnation has lower amount of acid sites than that prepared by SC impregnation. The NH₂⁺ signals are normalized by the weight of the catalysts and expressed in the unit of 10^{-3} mol NH₃/g-cat, and the values are displayed in Table S1.

The quantified acid sites of the samples after different treated conditions are summarized in Table 2. The acid number of fresh WZ(SC)/SBA-15 without Pt promoter is the highest, 1.41 mol NH₃/g-cat. Loading Pt on SBA-15 supported WZ catalysts leads to a decrease in NH₃ desorption signals. In comparison to the unsupported Pt/WZ, that supported on SBA-15 markedly enhances the acidity of the catalyst. The fresh Pt/WZ(SC)/SBA-15 has ~three times increase in the numbers of the acid sites (1.17 vs. 0.37 mol NH₃/g-cat). These results demonstrate that dispersion of WZ on SBA-15 can effectively increase the surface acidity, while deposition of Pt may cover-up a portion of acid sites.

After exposing the catalyst to the reaction mixture of n-pentane and hydrogen at 250°C for 1 hr, the acidity of WZ(SC)/SBA-15 decreases from 1.41 to 1.14 mol NH₃/g-cat. However, the acidity decreases only slightly from 1.17 to 1.12 mol NH₃/g-cat over Pt/WZ(SC)/SBA-15 after the same treatment. The gas pretreatment is to mimic the reaction condition of n-pentane isomerization in the presence of hydrogen. That is to say that after exposing the catalysts in the reaction atmosphere for 1 hr, the acid amount decreases 19.1% over WZ(SC)/SBA-15 without Pt promoter, whereas only 4.7% decrease over Pt/WZ(SC)/SBA-15. These results strongly evidence that Pt promoter can retain the acid sites, presumably by less formation of coke.

Pyridine adsorption/desorption observed by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy was performed to distinguish the acid sites on the catalysts to be Brønsted or Lewis in nature. Figure 10 shows the DRIFT spectra of WZ(SC)/SBA-15 and Pt/WZ(SC)/SBA-

TABLE 2 Acidities of Pt/WZ(SC), WZ(SC)/SBA-15, and Pt/WZ(SC)/SBA-15 determined by NH₃-TPD

| Sample | Pt/WZ(SC) | WZ(SC)/SBA-1 | 5 | Pt/WZ(SC)/SBA-15 | |
|--|-----------|--------------|---------------|------------------|-------------|
| Condition | Fresh | Fresh | $H_2 + C_5^a$ | Fresh | $H_2 + C_5$ |
| Acidity (×10 ⁻³ mol of NH ₃ /g) ^b | 0.37 | 1.41 | 1.14 | 1.17 | 1.12 |
| Loss of acidity after gas treatment (%) | - | - | 19.1 | - | 4.3 |

^aPrior to the NH₃-TPD experiments, the samples were heated in 10% H₂/Ar saturated with *n*-pentane at 250°C for 1 hr.

^bNH₂⁺ signals were determined by integration of the peak area between 150 and 500°C during desorption and normalized by per gram of the catalysts used.



FIGURE 10 In-situ DRIFT spectra of pyridine adsorbed on the fresh and pretreated catalysts. The pretreatment was done by exposing the catalysts to *n*-pentane/nitrogen with or without hydrogen, followed by heated at 250°C for 1 hr. The spectra were recorded after introduction of the pyridine vapor and evacuated at room temperature under 10^{-5} Torr

15 before and after pretreated either in *n*-pentane or in the mixture of *n*-pentane and hydrogen at 250° C for 1 hr, prior to the adsorption of pyridine. The spectra were recorded after exposing the pretreated catalysts to pyridine vapor for 30 min. at room temperature and then evacuated to 10^{-5} Torr. The peaks corresponding to pyridine adsorbed on Brønsted acid site (~1,541 and 1,638 cm⁻¹) or Lewis acid site (1,446 and 1,599 cm⁻¹) were observed on the catalysts, while the peak at 1,490 cm⁻¹ was attributed to pyridine associated with both Brønsted and Lewis acid sites.^[27–29] In comparison of the fresh catalysts WZ(SC)/SBA-15 and Pt/WZ(SC)/SBA-15, all these peaks are less intense on Pt loaded sample, in agreement with the NH₃-TPD results shown in Table 2. This observation also implies that Pt may cover both Brønsted and Lewis acid sites on WZ(SC)/SBA-15.

The gas pretreatment is to mimic the reaction condition of *n*-pentane isomerization. Nearly all the IR peaks of adsorbed pyridine on Brønsted and Lewis acid sites disappear, if only pretreating Pt/WZ(SC)/SBA-15 in *n*-pentane. If the mixture of *n*-pentane and hydrogen was used for pretreatment at 250°C, IR peaks of both Brønsted and Lewis acid sites were retained but the peak intensities were reduced. Moreover, the IR peaks of adsorbed pyridine on the Brønsted and Lewis acid sites shift slightly from 1,541 to 1,537 cm^{-1} and from 1,446 to 1,444 cm^{-1} , respectively. Similar phenomena were seen on both WZ (SC)/SBA-15 and Pt/WZ(SC)/SBA-15, although the peaks corresponding to Brønsted acid sites almost vanish for Pt/WZ(SC)/SBA-15. These results confirm that adding hydrogen into the reactant stream can effectively retard coke formation. Table 3 lists the consumption percentages of both acid sites after pretreatment with *n*-pentane and hydrogen. The losses in Brønsted and Lewis acid sites are 31.9 and 39.2%, respectively, over WZ(SC)/SBA-15, whereas 81.9 and 16.5% over Pt/WZ(SC)/SBA-15. It is, therefore, to say that Pt incorporation enhances the consumption of Brønsted acid sites but inhibits that of Lewis acid sites during *n*-pentane isomerization. These results infer that Pt may assist the generation of acid sites from hydrogen, which explains the promotion in conversion as compared to the case without hydrogen.

2.6 | Reaction mechanism of *n*-pentane isomerization over Pt/WZ/SBABA-15

Solid acids loaded with Pt are considered bifunctional catalysts in alkane isomerization.^[19] Pt owns the activity in hydrogenation/dehydrogenation. In this study, Pt is considered to be the site for hydrogen adsorption and dehydrogenation of *n*-pentane to form 2-pentene,^[30] as shown in Equations (1) and (2) of Scheme 1. Hydrogen molecules are considered to undergo heterolytic fission on Pt surface, and the generated proton and hydride spill-over to tungstate,^[19,30] as shown in Equation (3).

Protonation of 2-pentene should take place at the Brønsted acid sites on tungstate. Equation (4) illustrates that carbocation is formed and stabilized by the adjacent oxygen of the Brønsted acid sites. The carbocation generated in Equation (4) is a secondary carbocation, which tends to rearrange into a more stable tertiary carbocation through methyl migration (Equation 5). The tertiary carbocation combines with the hydride formed from **TABLE 3** Consumption of Brønsted and Lewis acid sites over WZ (SC)/SBA-15 and Pt/WZ(SC)/SBA-15 after pretreating in H₂ and *n*-pentane at 250°C for 1 hr

| Sample | WZ(SC)/ SBA-15 | | Pt/WZ(SC)/ SBA-15 | |
|-----------------------------|----------------|-------|-------------------|-------|
| Acide site | Brønsted | Lewis | Brønsted | Lewis |
| Loss in acid sites $(\%)^a$ | 31.9 | 39.2 | 81.9 | 16.5 |

^aBrønsted and Lewis acid sites were calculated based on the peak height at 1,541 and 1,446 cm⁻¹, respectively, using the intensity at 1,315 cm⁻¹ as the baseline.



SCHEME 1 Proposed mechanism of the *n*-pentane isomerization over Pt/WZ/SBA-15

heterolytic fission of H_2 to produce *iso*-pentane, as shown in Equation (6). The overall reaction mechanism of the *n*-pentane isomerization over the Pt/WZ/SBABA-15 catalyst is shown in Scheme 1.

Triwahyono et al.^[31] investigated the effects of hydrogen on acid sites of WO₃-ZrO₂ and Pt/WO₃-ZrO₂. In the presence of hydrogen, the number of Brønsted acid sites was reported to increase and that of Lewis acid sites decrease as the temperature was raised from 25 to 120°C. In the present study, in-situ IR experiments (Figure 10) show that Brønsted acid sites on the Pt/WZ(SC)/SBA-15 catalyst are nearly consumed, while the ones on the WZ (SC)/SBA-15 catalyst without Pt promoter still have a portion remained after the pretreatment in hydrogen and *n*-pentane. It is also noted that the consumption of Brønsted acid sites is more apparent than that of Lewis acid sites over Pt-promoted WZ(SC)/SBA-15 (Table 3). Such spectral observations suggest that Brønsted acid sites are the catalytic active centers for *n*-pentane isomerization and the de-protonated acid sites can be regenerated by the protons produced on the surfaces of Pt from heterolytic fission of H₂. It explains that addition of hydrogen $(2 \sim 10 \text{ ml/min})$ not only increases the conversion of *n*pentane, but also enhances the stability of the catalytic performance (Figure 7). In contrast, a fast decline of conversion and selectivity was seen in the absence of JOURNAL OF THE CHINESE CHEMICAL SOCIETY

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hydrogen, probably due to that the de-protonated acid sites cannot be efficiently regenerated. However, the conversion is leveling-off when too much hydrogen is added into the reactant stream, attributed to that the dehydrogenation of pentane (Equation 2) is inhibited. Instead, hydrogenolysis of pentane becomes a competing process.

3 | EXPERIMENTAL

3.1 | Catalysts preparation

SBA-15 was synthesized following the method reported by Zhao et al.^[32] Four grams of the Pluronic triblock copolymer (P123, $M_n = 5,800$) was dissolved in 160 ml of 2 M HCl solution. After adding 8.4 g of tetraethyl orthosilicate, the solution was stirred at 35°C for 24 hr, followed by the hydrothermal treatment at 90°C for another 24 hr. The assynthesized SBA-15 powders were collected by filtration and dried at 100°C overnight. Finally, the samples were calcined at 560°C for 6 hr (ramping rate of 1°C/min) to remove the organic templates.

Tungstated zirconia deposited on SBA-15 was achieved by conventional and SC impregnation. The conventional impregnation method was based on the procedures described by Li et al.^[6] SBA-15 powders were dispersed in a methanol solution of zirconium(IV) acetylacetonate under vigorous stirring. An aqueous solution of ammonium metatungstate hydrate was added and stirred for 1 hr. After removing the solvent in a rotary evaporator, the solid was dried at 100°C overnight and calcined at 800°C for 3 hr with a ramping rate of $1^{\circ}C/$ min (Figure S1). The resulted sample is labeled "Im" in the bracket. For SC impregnation, a 50 ml beaker conthe aforementioned taining slurry of SBA-15, zirconium(IV) acetylacetonate/water and ammonium metatungstate hydrate/methanol was transferred to a 600 ml autoclave containing 150 ml of 99.5% ethanol. The autoclave was then heated at 270°C for 3 hr. Under such a condition, ethanol should achieve SC condition in the high pressure Parr reactor. After cooling down to room temperature, the solid products were collected by filtration and dried at 100°C overnight. After calcination at 800°C for 3 hr, the impregnated samples were obtained and denoted as "SC" for discrimination. A further optimization of WO₃ and ZrO₂ loadings was included in this study. Pt-deposition on WZ/SBA-15 was obtained by conventional impregnation. The samples were suspended in an aqueous solution of platinum(IV) chloride, dried at 100°C overnight, and calcined at 500°C for 3 hr (ramping rate 2° C/min).

To elucidate the sole effect of WO₃, SBA-15 supported tungsten oxide was prepared by SC impregnation, and termed as W(SC)/SBA-15. The composition of the sample was 20 wt% WO₃ and 80 wt% SBA-15. As a control, WZ without SBA-15 support was also prepared by SC impregnation, and named as WZ(SC), of which the composition was 20 wt% WO₃ and 80 wt% ZrO₂.

3.2 | Catalyst characterization

Powder X-ray diffraction (PXRD) patterns were recorded with a Panalytical X'Pert diffractometer using Cu Ka radiation in an operating mode of 45 kV and 40 mA. Nitrogen physisorption was carried out in a Micromeritics TriStar 3000 system. Prior to the physisorption, 0.1 g of the sample was degassed at 200°C under 10⁻³ Torr for at least 8 hr. Acidity of the catalysts was determined by TPD of NH₃ using an AutoChem 2910 system with a Thermo ONIX ProLab guadrupole detector. 0.25 g of the sample was heated in a 50 ml/min of He flow at 500°C for 1 hr to remove the adsorbed moisture. Three percentage of ammonia in He (50 ml/min) was introduced to the sample at 100°C for 1 hr, followed by purging the sample with pure He (30 ml/min) for another hour. While the sample was heated to 800° C with a ramping rate of 10° C/ min, the NH_2^+ (m/z = 16) signal from the effluent was recorded with a quadrupole mass spectrometer.

Adsorption of pyridine was used to distinguish Brønsted and Lewis acid sites by in situ DRIFTS. The adsorption-desorption of pyridine over the samples was conducted in an in-situ sample cell (Harrick) using a BOMEM MB155 FT-IR spectrometer. The resolution of the recorded spectra is 4 cm⁻¹. 0.1 g of the sample was pressed into a disk and placed inside the cell. After heated at 200°C under 10^{-5} Torr for 3 hr and cooled down to room temperature, the sample was exposed to pyridine vapor for 30 min and evacuated to 10^{-5} Torr for another 30 min to remove pyridine vapor in the gas phase. The IR spectra were recorded under 10^{-5} Torr while elevating the temperature to 500° C.

3.3 | Catalytic test of *n*-pentane isomerization

Isomerization of *n*-pentane was performed in a fixed-bed reactor at atmospheric pressure. Prior to the reaction,

0.5 g of the catalyst was packed into the reactor and pretreated in dry air at 450° C for 3 hr, followed by cooling down to 250° C in a nitrogen flow. The reactants stream containing *n*-pentane, hydrogen and nitrogen (0.37: 2: 10 ml/min) flew through the catalyst bed in a weight hourly space velocity (WHSV) of 1,484.4 ml/g_{cat}-h. The products were separated and analyzed by a gas chromatog-raphy (Shimadzu 14A), equipped with a capillary column (RTX-1, 60 m), and a flame ionization detector. Heating the sample in an air stream at 450° C for 6 hr was conducted to regenerate the used catalyst.

The *n*-pentane conversion as well as product selectivities and yields were calculated based on the following equations.

Conversion (%) = (inlet moles – outlet moles of
$$n$$
 – pentane)
/(inlet moles of n – pentane) × 100
(1)

Selectivity (%) = (moles of specific product) /(inlet moles – outlet moles of n – pentane) × 100

(2)

Yield (%) = Selectivity of specific product

$$\times n$$
 - pentane conversion $\times 100$ (3)

4 | CONCLUSIONS

Well dispersed WZ supported on SBA-15 was prepared by impregnation in SC ethanol. In comparison with the catalyst prepared by conventional impregnation, better dispersion of WZ on SBA-15 support was achieved by the SC treatment. The optimal catalytic activity was achieved on Pt/WZ(SC)/SBA-15 catalyst with the loading ratio of WO₃/ZrO₂/SBA-15 in 20/40/40 wt%, which corresponds to the surface concentration of 2.4 W-atoms/nm² and 8.9 Zr-atoms/nm². The nearly monolayer dispersion of WO₃ leads to catalysts of high surface areas and pore volumes because the blockage or filling the pore channels of SBA-15 by bulk WO₃ particles is avoided.

Infrared spectroscopic investigations showed that Brønsted acid sites on WZ/SBA-15 catalyst were the active centers for *n*-pentane isomerization. With 1 wt% Pt as the promoter, the SBA-15 supported WZ prepared by SC impregnation gave 66% *n*-pentane conversion and 99% selectivity of *iso*-pentane. The role of Pt is considered to enhance the dehydrogenation of *n*-pentane. However, the pentane conversion decreased rapidly after ~5 hr onstream. Introduction of hydrogen (2 ~ 10 ml/min, or 0.016 ~ 0.08 MPa) into the gas stream of reactants was found to markedly inhibit the decay of the catalytic activities. Infrared spectroscopic studies showed that the acidic sites were retained in the presence of hydrogen. Therefore, hydrogen was proposed to be dissociated on the surface of Pt through heterolytic fission to form proton and hydride. The proton regenerated the acid site, which was consumed in isomerization and consequently retarded the deactivation of the solid acid catalysts. Overdosing hydrogen (10 ml/min, 0.08 MPa) leaded to a leveling-off in conversion of *n*-pentane, accompanying with generation of more cracking products from hydrogenolysis of alkanes and lowered iso-pentane selectivity.

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REFERENCES

- [1] A. Corma, A. Martinez, Catal. Rev.-Sci. Eng. 1993, 35, 483.
- [2] G. Yaluris, R. B. Larson, J. M. Kobe, M. R. Gonzalez, K. B. Fogash, J. A. Dumesic, J. Catal. 1996, 158, 336.
- [3] a)M. Hino, K. Arata, Chem. Commun. 1988, 1259 b) B. H. Davis, R. A. Keogh, R. Srinivasan, Catal. Today 1994, 20, 219.
- [4] M. Hino, K. Arata, Chem. Commun. 1980, 851.
- [5] K. Arata, Adv. Catal. 1990, 37, 165.
- [6] T. Li, S. T. Wong, M. C. Chao, H. P. Lin, C. Y. Mou, S. Cheng, Appl. Catal., A 2004, 261, 211.
- [7] Q. H. Xia, K. Hidajat, S. Kawi, Chem. Commun. 2000, 2229.
- [8] C. L. Chen, S. Cheng, H. P. Lin, S. T. Wong, C. Y. Mou, Appl. Catal., A 2001, 215, 21.
- [9] S. T. Wong, T. Li, S. Cheng, J. F. Lee, C. Y. Mou, J. Catal. 2003, 215, 45.
- [10] A. Baiker, Chem. Rev. 1999, 99, 453.
- [11] K. Chhor, J. F. Bocquet, C. Pommier, Mater. Chem. Phys. 1992, 32, 249.
- [12] H. Hayashi, K. Torii, J. Mater. Chem. 2002, 12, 3671.
- [13] J. Morère, M. J. Tenorio, M. J. Torralvo, C. Pando, J. A. R. Renuncio, A. Cabanas, J. Supercrit. Fluids 2011, 56, 213.
- [14] S. R. Vaudagna, S. A. Canavese, R. A. Comelli, N. S. Figoli, Appl. Catal., A 1998, 168, 93.
- [15] D. Y. Zhao, J. L. Feng, Q. S. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, Science 1998, 279, 548.
- [16] F. D. Rossini, E. J. R. Prosen, K. S. Pitzer, J. Res. Natl. Inst. Stand. Technol. 1941, 27, 529.
- [17] R. Kourieh, S. Bennici, M. Marzo, A. Gervasini, A. Auroux, Catal. Commun. 2012, 19, 119.
- [18] N. Naito, N. Katada, M. Niwa, J. Phys. Chem. B 1999, 103, 7206.
- [19] A. H. Zhang, I. Nakamura, K. Aimoto, K. Fujimoto, Ind. Eng. Chem. Res. 1995, 34, 1074.
- [20] Y. Ono, Catal. Today 2003, 81, 3.
- [21] M. Khurshid, M. A. Al-Daous, H. Hattori, S. S. Al-Khattaf, Appl. Catal., A 2009, 362, 75.
- [22] J. C. Yori, J. C. Luy, J. M. Parera, Appl. Catal. 1989, 46, 103.
- [23] B. H. Li, R. D. Gonzalez, Appl. Catal., A 1997, 165, 291.

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- [24] S. De Rossi, G. Ferraris, M. Valigi, D. Gazzoli, Appl. Catal., A 2002. 231. 173.
- [25] Z. S. Hou, B. X. Han, J. M. Zhang, Z. M. Liu, J. He, X. G. Zhang, G. Y. Yang, J. Supercrit. Fluids 2003, 25, 81.
- [26] C. D. Baertsch, S. L. Soled, E. Iglesia, J. Phys. Chem. B 2001, 105, 1320.
- [27] C. A. Emeis, J. Catal. 1993, 141, 347.
- [28] Y. Li, W. H. Zhang, L. Zhang, Q. H. Yang, Z. B. Wei, Z. C. Feng, C. Li, J. Phys. Chem. B 2004, 108, 9739.
- [29] J. M. Campelo, D. Luna, R. Luque, J. M. Marinas, A. A. Romero, J. J. Calvino, M. P. Rodriguez-Luque, J. Catal. 2005, 230, 327.
- [30] Y. Ono, M. Taguchi, S. Gerile, S. Suzuki, T. Baba, Stud. Surf. Sci. Catal. 1985, 20, 167.
- [31] S. Triwahyono, T. Yamada, H. Hattori, Appl. Catal., A 2003, 242, 101.
- [32] D. Y. Zhao, Q. S. Huo, J. L. Feng, B. F. Chmelka, G. D. Stucky, J. Am. Chem. Soc. 1998, 120, 6024.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article. **How to cite this article:** Lee W, Yang C-C, Cheng S. Isomerization of *n*-pentane over platinum promoted tungstated zirconia supported on mesoporous SBA-15 prepared by supercritical impregnation. *J Chin Chem Soc.* 2021;68:409–420. https://doi.org/10.1002/jccs.202000473