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Pt–Sn-Based SAPO-34 Supported Novel Catalyst for *n*-Butane Dehydrogenation

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The performance of Pt–Sn/SAPO-34 novel catalyst was investigated for *n*-butane dehydrogenation. The catalyst was characterized by number of physicochemical techniques X-ray fluorescence (XRF), X-ray diffraction (XRD), ammonia temperature-programmed desorption (NH₃-TPD), hydrogen temperature-programmed reduction (H₂-TPR), temperature-programmed oxidation (TPO), transmission electron microscopy (TEM), and O₂-pulse coke measurement. The metallic contents, structure, acidity, and metallic dispersion were determined in order to explain catalyst superiority and functionality using SAPO-34 as support. Pt–Sn-based SAPO-34 supported catalyst was parametrically characterized in order to obtain superior control of dehydrogenation reaction stereochemistry. Above 91% of total olefins with 80% butene was achieved over Pt–Sn/SAPO-34. The weight hourly space velocity 2.8 h⁻¹ and temperature 585 °C were found to be optimum for the higher dehydrogenation activity. The catalysts also showed very good hydrothermal stability in continuous reaction–regeneration cycles. The coke formation was mainly related to catalyst activity.

Introduction

Propene and butenes are the most valuable byproduct of steam cracking and fluid catalytic cracking (FCC) units.^{1–4} These conventional methods of light olefin production fail to meet the rapidly growing demand.⁴ Altogether 39 million tons of butene was produced in 2008, and the current demand for it is much higher.⁵ Moreover, paraffins are the world's most abundant hydrocarbon resource and a versatile class of feedstock to produce olefins. The output of the butane fraction has been about 150–200 million tons each year.^{1,6} The introduction of non-petroleum based routes (intentional technologies) have currently become popular.⁴ Paraffin dehydrogenation was observed to be the most economical option to produce light olefins.^{3,4,7} These processes are projected to yield 14% of the global supply of olefins by 2010.⁸

Dehydrogenation of butanes was first developed and commercialized at Leuna in Germany, using a chromia–alumina catalyst designed by UOP (then Universal Oil Products) in the USA together with ICI, England.⁹ Both Pt and Cr supported alumina catalysts were extensively studied, while their performance for light alkane dehydrogenation was still unsatisfactory.^{3,10–19} Quick deactivation and excessive coke formation were the prominent drawbacks of alumina-supported catalysts.²⁰ Recently, environmentally friendly and noncorrosive, solid acid catalysts, zeolites and zeolite-based catalysts, have become famous in the petrochemical industry due to their unique properties.²¹ Recently direct butane dehydrogenation was focused on as an oxidative method having serious processing and operating problems.^{3,18} Direct dehydrogenation is an endothermic reaction that requires relatively high temperatures and low pressures. This high process temperature favors side-reactions and generates coke precursors. Hence, a more robust catalyst that has better control over the stereochemistry of the butane dehydrogenation reaction is needed.

Previously Pt–Sn/ZSM-5 was extensively studied for propane dehydrogenation to propylene, while much attention has been given to metallic content modifications and combinations.^{3,22–24}

The role of Pt–Sn was also characterized in a number of studies.^{24–28} It was observed that the intensification of the support has a more dominant influence on the performance of the dehydrogenation reaction than metallic modifications.³ It was also reported that the prereaction with hydrogen decreases the coke formation and enhances dehydrogenation activity without influencing the secondary reaction of light olefin production.^{3,19} As *n*-butane contains both primary and secondary carbon atoms, so the dehydrogenation was normally explained by penta-coordinated carbonium ion intermediates formed over Brønsted acid sites. No study has been focused on *n*-butane dehydrogenation to produce light olefins using a novel catalyst supported on SAPO-34.

In this paper *n*-butane dehydrogenation over Pt–Sn/SAPO-34 was investigated to produce light olefins, particularly butenes. The catalyst was characterized using a number of physicochemical techniques and parametrically characterized in order to understand the reaction dynamics.

Experimental Section

Catalyst Preparation. The SAPO-34 catalyst was prepared first by mixing Al₂O₃:P₂O₅:SiO₂:TEA:H₂O in a molar ratio 1:1:0.5:2:100.²⁹ The solution was stirred to make a uniform mixture and then aged for 24 h at room temperature. Later the solution was autoclaved at 200 °C under autogenous pressure. After 24 h, the product was filtered, dried, and calcined at 550 °C for 4 h (BET surface area 479 m²/g). The monometallic catalyst Pt/SAPO-34 was prepared at 70 °C by coimpregnation.³ The prepared powder SAPO-34 was impregnated with a 0.03 M H₂PtCl₆ aqueous solution, and their amount was fixed to maintain 0.5 wt % Pt content in the final product. After impregnation, the catalyst was dried at 100 °C for 3 h and then calcined at 500 °C for 4 h. The Pt–Sn/SAPO-34 catalyst was prepared by a sequential impregnation method.³ The SAPO-34 was first impregnated with promoter Sn:0.16 M SnCl₂·2H₂O aqueous solution at 80 °C in order to ensure 1 wt % Sn content in the final catalyst. After the impregnation, the catalyst was dried at 100 °C for 3 h and finally calcined at 500 °C for 4 h. Then Sn/SAPO-34 catalyst was coimpregnated again with Pt: 0.03 M H₂PtCl₆ aqueous solution at 70 °C. Afterward the catalyst was dried at 100 °C for 3 h and calcined at 500 °C for

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4 h. Pt–Sn/ZSM-5 was also prepared in similar manner using powdered ZSM-5 of a Si/Al ratio of 140. The catalysts were used in pure form without pelletization.

Catalysis Characterization. The catalysts were characterized using number of physiochemical techniques. The metallic contents of prepared samples were verified using X-ray fluorescence (XRF) on a Shimadzu XRF 1700 fluorimeter. The X-ray diffraction (XRD) patterns of catalysts were obtained using a powder X-ray diffractometer (Rigaku-2500), in order to ensure texture of support. The XRD studies were performed with Cu K α radiation, and the X-ray tube was operated at 40 kV. The spectra were scanned at a rate of 5°/min, from 5° to 35° (an angular range 2 θ). The BET surface area of catalysts was measured using N₂ adsorption/desorption isotherms and determined using an automatic analyzer (Autosorb-1-C). The surface areas of catalysts were calculated using the BET equation.

The acid properties of Pt–Sn/SAPO-34 catalyst were determined by ammonia temperature-programmed desorption (NH₃-TPD), using an Autochem-II 2920 analyzer. The catalyst samples were treated first by flowing dry argon at 500 °C for 1 h and then passed ammonia for adsorption at room temperature. Later the temperature was kept at 100 °C for 0.5 h to desorb the physically adsorbed ammonia. The temperature was raised to 600 °C with a heating rate of 10 °C/min and ammonia desorption profile was recorded by thermal conductivity detector. Temperature-programmed reduction (TPR) was carried out on a similar setup as used for NH₃-TPD. The samples (0.2 g) were dried first for 1 h at 500 °C and then heated to 800 °C (at a heating rate 10 °C/min). The 5% (v/v) H₂/N₂ mixture was used as reducing gas. Hydrogen consumption as a function of reduction temperature was recorded.

The temperature-programmed oxidation (TPO) for coke analysis was carried out using reacted catalyst (0.2 g). The sample was purged in a N₂ flow (40 mL/min) at 500 °C for 30 min. Then, the temperature was slowly decreased to 25 °C prior to the TPO experiment. A mixture of 2% oxygen and 98% helium by volume was passed through the samples at the flow rate of 40 mL/min. The temperature was ramped up at 10 °C/min and the CO₂ generated was monitored by an online gas analyzer QIC-20 (HIDEN, England). The Pt metal dispersion was also verified before and after the reaction test by transmission electron microscope equipped with energy dispersive spectroscopy. The amount of coke was measured by O₂-pulses using a thermal conductivity detector (TCD) at 700 °C. The injecting pulses of pure oxygen (99.99%) were continued until deposited coke was fully removed. The CO₂ formed was continuously measured, and the amount of coke formed was calculated.

Catalyst Performance Evaluation. The catalytic performance of Pt–Sn/SAPO-34 novel catalyst for *n*-butane dehydrogenation to butane and light olefins was investigated in a continuous plug-flow quartz microreactor at atmospheric pressure. In the present study, 99.95% *n*-butane was used as the feed provided by Zhong Ke Hui Jie (HJAT), Beijing, China. The measured amount of samples was loaded into the reactor in order to maintain the desired weight hourly space velocity (WHSV) at 2.8 h⁻¹. Before the reaction test, each catalyst was first reduced under flowing H₂ (7.5 mL/min) at 500 °C for 10 h. The reaction mixture was composed of H₂/C₄H₁₀ (molar ratio 0.25), and product compositions were continuously recorded by an online gas chromatograph

Table 1. Basic Catalyst Characteristics

catalysts	Pt content (% w/w) ^a	Sn content (% w/w) ^a	S_{BET} (m ² /g) ^b
SAPO-34			479
Pt(0.5 wt %)–Sn(1 wt %)/SAPO-34	0.43	0.86	418

^a Results from XRF analysis. ^b Calculated from N₂ physisorption using the BET equation.

(GC7890II) equipped with a flame ionization detector (FID). All the given values were in weight percentages.

Hydrothermal analysis of the Pt–Sn/SAPO-34 catalyst was carried out in the same reactor for up to three consecutive runs; each of 8 h. The catalyst was regenerated at 600 °C for 4 h with a nitrogen–steam mixture (40 mL/min) and a steam partial pressure of 20 kPa. After regeneration, the catalysts were dried in flowing nitrogen for 30 min and then reduced in hydrogen at 500 °C before the next reaction. The similar operating procedure was adopted for next experimental run.

Results and Discussion

Catalyst Characterization. At first, the metallic incorporation was confirmed by using XRF analysis (see Table 1). It was observed that metals were successfully doped on the support by the sequential impregnation method. The surface area of the prepared support SAPO-34 and that after metallic doping were calculated and shown in Table 1. The result shows that after metallic doping the BET surface area was decreased. The BET surface area of the Pt(0.5 wt %)–Sn(1 wt %)/SAPO-34 catalyst was 418 m²/g. This decline in surface area was due to the metals existence over the surface of the support. From the X-ray diffraction patterns of the SAPO-34 and SAPO-34 supported catalysts, it was observed that the metal incorporation did not destroy the structural topology and texture of SAPO-34 support. Therefore, the patterns were identical and results were not presented here. As the average diameter of Pt particles was in the ranges of 1.4–2.5 nm and did not diffuse into the SAPO-34 small pores of maximum size 0.46 nm.^{3,30,31}

The dehydrogenation activity of each catalyst was associated with its acidic properties. Therefore the acidities of both SAPO-34 (support) and Pt–Sn/SAPO-34 (catalyst) were analyzed by NH₃-TPD. The decline in Brønsted acid sites was observed after metallic incorporation, while it was not fully consumed. This weak acidity suitably converts intermediates and enhanced olefin selectivity. The reduction properties of the novel catalyst Pt–Sn/SAPO-34 was measured by H₂-TPR and shown in Figure 1. It has long been known that pure zeolites did not show reduction peaks. On the other hand, Pt–Sn/SAPO-34 catalyst showed reduction peaks at lower (<250 °C) and higher temperatures (>435 °C). A similar trend was reported in some previous studies.^{24,32} The reduction peak at the higher temperature indicated that the Pt was interacted with well on SAPO-34 in the presence of Sn.^{24,30–32}

From TPO results, it was further observed that the coke was not deposited on the Pt but on the support, which stabilizes the catalyst's activity for longer runs (see Figure 2). In TPO, the profile peak at higher temperatures indicates that coke is deposited on the support,²⁴ while the peak height represents the intensity of deposition. The TEM image of Pt–Sn/SAPO-34 catalyst before and after the reaction shown in Figure 3a and b, respectively, proves that the presence of Sn prevents

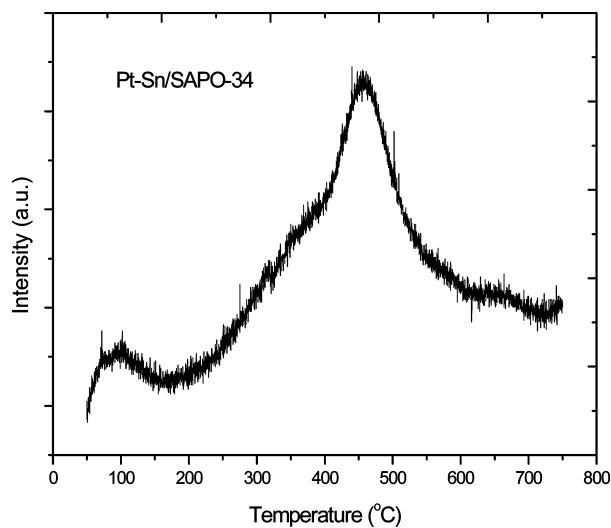
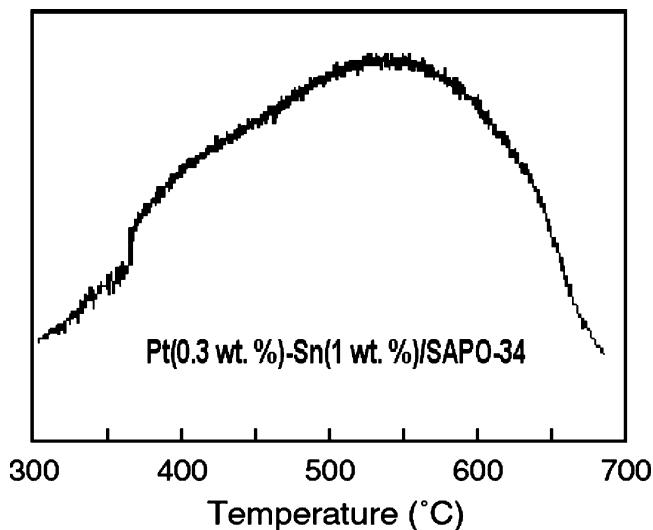
Figure 1. $\text{H}_2\text{-TPR}$ profile of the Pt–Sn/SAPO-34 catalysts.

Figure 2. TPO profile of the Pt–Sn/SAPO-34 catalysts after 8 h reaction test.

sintering. The agglomerations of Pt particles were not found in both images before and after the reaction.

Catalyst Performance Analysis. It is obvious from the reaction test that support SAPO-34 has very low conversion, less than 3 wt %. This result suggests that the support was inert toward cracking and dehydrogenation of *n*-butane due to weak surface acidity. It has long been known that higher acidities were needed for dehydrogenation, which is true, but in that case, cracking was also promoted simultaneously. In order to avoid this type of situation and to make the catalysts more selective and robust toward dehydrogenation, SAPO-34 was selected as a support for metallic incorporation, so that the metal actively abstracts hydrogen from paraffins and later the weak acid sites provided by the support selectively convert intermediates into light olefins.

The performance of a Pt/SAPO-34 catalyst shows better conversion and butene selectivity, with higher total olefins selectivity, than SAPO-34 (see Table 2 and Figure 4). While Pt–Sn/SAPO-34 demonstrates more superior conversion (initial conversion 36%) and about 80% butene selectivity with about 92% total olefin selectivity. The results were shown in Figure 4. The initial lower butene selectivity of butane and higher conversion of *n*-butane was due to

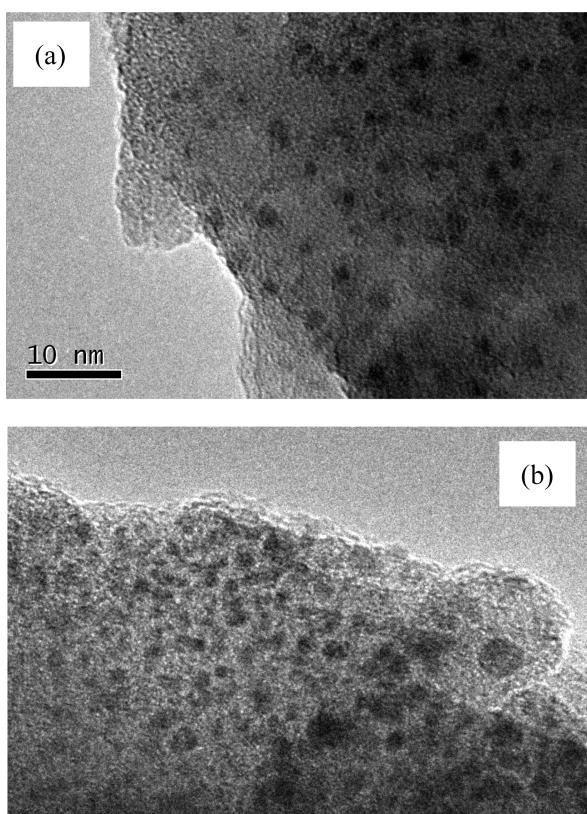
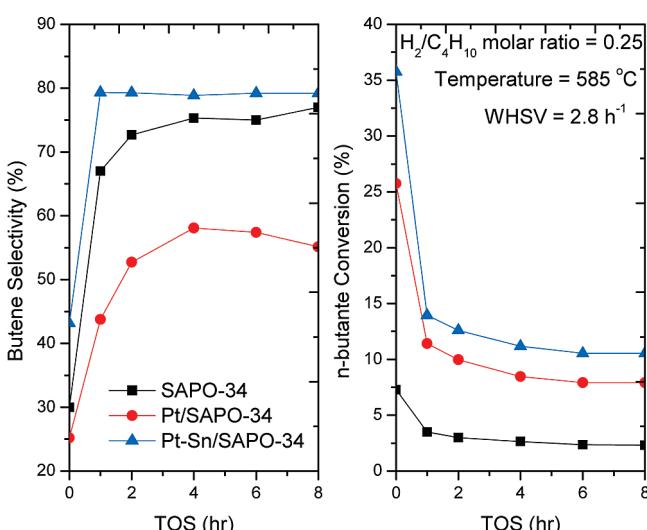


Figure 3. TEM images of Pt–Sn/SAPO-34 catalyst (a) before and (b) after the 8 h reaction.

Table 2. Deactivation as a Function of Different Pt–Sn Metallic Content Loaded on SAPO-34^a

catalysts	X_0	X_f	D_r	coke ^b	olefins
SAPO-34	7.5	2.9	4.6	0.25	83.2
Pt(0.5 wt %)-Sn(1 wt %)/SAPO-34	36.1	13.2	22.9	0.53	92.7

^a The deactivation parameter was defined as $D_r = [(X_0 - X_f)/X_0] \times 100$; where, X_0 is the initial conversion at 1 min, X_f is the final conversion, and S_f is the final selectivity at 8 h. The reaction temperature was 585 °C. ^b O₂-pulse coke analysis.

Figure 4. *n*-Butane dehydrogenation over SAPO-34, Pt/SAPO-34, and Pt–Sn/SAPO-34 catalysts.

cracking. Later the reaction shifts toward dehydrogenation, and butene will become a major product. This drastic enhancement in selectivity was not only due to the support

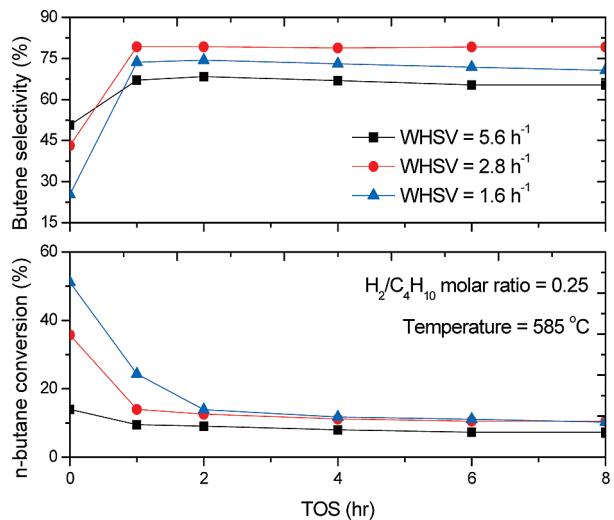


Figure 5. *n*-Butane conversion and butene selectivity at different WHSV values.

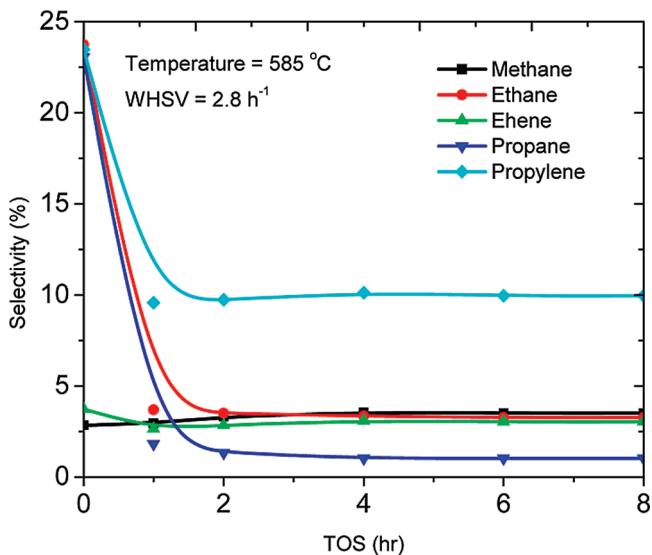


Figure 6. Product distribution over Pt–Sn/SAPO-34 at the optimum WHSV 2.8 h⁻¹ and 585 °C.

control on intermediates conversions but also due to better Pt dispersion and interaction with the support in the presence of Sn (see the Characterization section). The selective control of stereochemistry was more important than conversion in this reaction, as if the cracking products methane, ethane, and propane will become selective, it is more difficult to convert them into olefins.³³

Table 2 shows the activity decay and final total olefin selectivity at a time-on-stream of 8 h for SAPO-34 and Pt–Sn/SAPO-34. The deactivation rate was calculated using the relationship $D_r = [(X_0 - X_f)/X_0 \times 100]$, where X_0 is the initial *n*-butane conversion at 1 min and X_f is the final conversion at 8 h. It was observed that the catalyst deactivation was due to coke formation, while it was further observed that this coke amount was particularly related to catalyst activity (feed conversion).

In order to obtain the suitable catalyst to feed ratio, the important operating parameter weight hourly space velocity (WHSV) was examined and results were shown in Figure 5. It was observed that the lower WHSV (higher catalyst to feed ratio) enhanced *n*-butane conversion. While a decrease in WHSV from 2.8 h⁻¹ adversely affected the butene

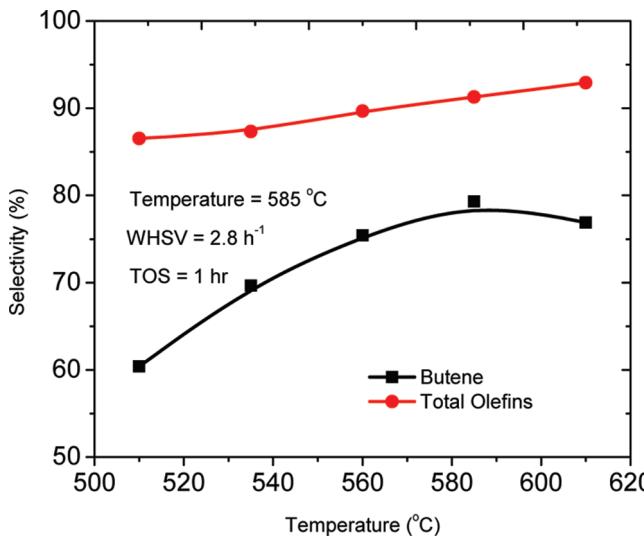


Figure 7. Influence of temperature on butene total olefin selectivity using Pt–Sn/SAPO-34.

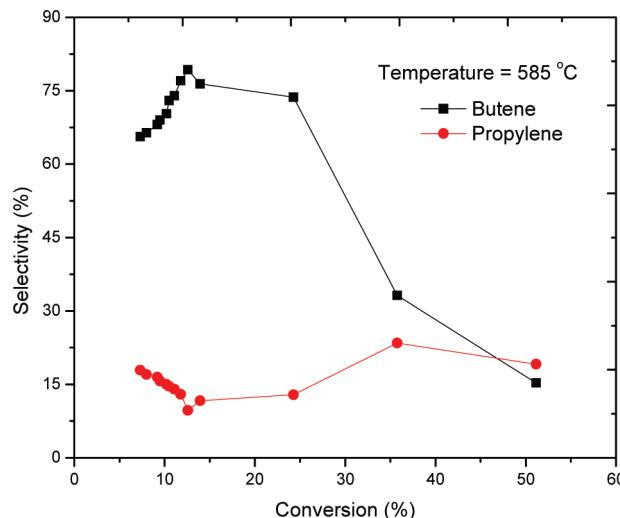


Figure 8. Olefin selectivity with conversion using Pt–Sn/SAPO-34.

selectivity, higher WHSV values favored propylene selectivity. Moreover lower WHSV values also favored parafin formation. Therefore, the optimum control of catalyst was observed at a WHSV of 2.8 h⁻¹, and this product distribution was shown in Figure 6. It was noted that initially the cracking products were selective and with time-on-stream (TOS), even after 1 h, the dehydrogenation become selective. Initially propylene selectivity was higher; therefore, the total olefins will remain high throughout the reaction. While some paraffins like ethane and propane were also among the cracking products, their selectivity was largely reduced with TOS to less than 4% and 2%, respectively.

It can be observed from Figure 7 that the selectivity of butene rapidly increased with an increase in the reaction temperature up to 585 °C (i.e., about 80%). The total olefin selectivity was continuously increased with the temperature. An above 90% total olefin selectivity was achieved above 585 °C over Pt–Sn/SAPO-34 at a WHSV of 2.8 h⁻¹. The yields of total olefins and butene were also continuously increased with the rise in temperature owing to a distinct increase in conversion. The maximum value of the butene yield was 14% at 585 °C and at a TOS of 1 h.

Table 3. Catalyst Performance in a Continuous Operation for Three Consecutive Runs at WHSV = 2.8 h⁻¹ and 585 °C (Regenerated with Steam)

Pt–Sn/ZSM-5 at varying TOS	run I		run II		run III	
	TOC (%)	conv (%)	TOC (%)	conv (%)	TOC (%)	conv (%)
1 h	91.8	14.1	91.9	13.9	92.1	13.8
8 h	92.7	13.2	92.6	13.2	92.9	13.1

Table 4. Support Influence on Pt–Sn Catalyst Performance for n-Butane Dehydrogenation at WHSV = 2.8 h⁻¹, TOS = 1 h, and 585 °C

catalysts	Pt–Sn/ZSM-5	Pt–Sn/SAPO-34
butene selectivity (%)	19.1	80.1
propylene selectivity (%)	12.4	9.9
total olefins selectivity (%)	52.1	91.7
n-butane conversion (%)	56.7	14.8

The highest butene selectivity was achieved between 12–14% conversion as observed from Figure 8. The reaction mechanism could be speculated from the product distribution as shown in Figures 4 and 6. Over Pt–Sn/SAPO-34, the first hydrogen was abstracted by a reduced metal site at the β -carbon of *n*-butane which form propoxy species. These propoxy species (intermediates) were selectively converted to butene by abstracting other hydrogens. This second hydrogen was abstracted by a framework oxygen of the support (SAPO-34).

Catalysis Stability in a Continuous Operation (Hydrothermal Study). Table 3 shows *n*-butane conversion over Pt–Sn/SAPO-34 catalyst and total olefin selectivity for three continuous runs at 585 °C and 2.8 h⁻¹ WHSV. The fresh catalyst exhibits the highest conversion. Before the second run, the catalyst was regenerated with nitrogen mixed steam for 5 h at 650 °C and then reduced in a hydrogen environment again. Similar results were achieved in the second and third runs after consecutive regenerations. These results proved the catalyst's stability on experimental grounds. The slight increase in total olefin conversion was noted due to decrease in the corresponding conversion of *n*-butane. The structure and acidic properties of SAPO-34 depend on the number and distribution of Si in the framework and make it stable during hydrothermal treatment. These facts give superiority to the SAPO-34 support over ZSM-5, where dealumination occurs frequently.²⁵

Comparison of Pt–Sn-Based Catalyst Supported on SAPO-34 and ZSM-5. Table 4 clearly demonstrates the superiority of the SAPO-34 supported Pt–Sn-based catalyst for *n*-butane dehydrogenation over ZSM-5 supported catalyst.

Conclusion

A superior *n*-butane dehydrogenation to butene was obtained using Pt–Sn/SAPO-34 novel catalyst. The catalyst functionality was characterized experimentally and by a number of physicochemical techniques. The structural topology of the support was ensured after metallic incorporation by XRD. The acid profiles confirm the acid site availability, even though some of the Brønsted acid sites were consumed during metallic interaction. Above 91% total olefin selectivity and above 80% butene selectivity were obtained over Pt–Sn/SAPO-34 up to 8 h of operation. It was noted that the higher WHSV favored propylene selectivity and WHSV values lower than 2.8 h⁻¹ promoted hydrogen transfer reactions due to the higher catalyst to feed ratio. It was further noted from the product distribution profile that the initial higher conversion was due to the higher cracking rate. The coke formation was an inherent problem related to the catalyst activity. The exceptional control of stereochemistry

was noted to produce olefins using Pt–Sn/SAPO-34 at 585 °C and WHSV 2.8 h⁻¹. The higher butene selectivity was obtained between 12 and 14% conversions. The catalyst stability was further verified under mild hydrothermal treatment during three consecutive runs. It was found that the catalyst activity and selectivity were stable after regeneration.

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