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n-Butane isomerization on sulfated zirconia: the effect of nonspecific olefin addition

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Abstract

Butene has been suggested to be an intermediate in the proposed bimolecular mechanism for *n*-butane isomerization over sulfated zirconia (SZ). The addition of butene has been shown to significantly increase the rate of this reaction. The question can be asked as to whether other olefins would affect this reaction as well. In this study, the effects of propylene, 1-butene and 1-pentene addition on the reaction induction period and selectivity were studied and compared at 100 and 150 °C. Enhanced catalyst activity was found for all three olefins. There was an optimum concentration of added olefin for maximum activity. Catalyst activity increased and the induction period decreased with increased olefin concentration. Adding any of the three olefins for only the initial 2 min of reaction caused a long-term positive impact on the reaction rate and isobutane selectivity, reinforcing our earlier proposed concept of "olefin-modified sites." The ratio of excess isobutane molecules formed per molecule of olefin added during the initial 2 min was around 14 at 100 °C and 692 at 150 °C for all three olefin additions. It is suggested that C_8^+ intermediates (part of the hypothesized bimolecular reaction pathway) are not the only oligomers leading to the selective product; the reaction appears to proceed through the formation of C_7^+ and C_9^+ oligomers as well. The results of this study clearly show that isobutane can be made equally well by a mechanism involving *n*-butane and olefins different from butene.

Keywords: Sulfated zirconia; *n*-Butane isomerization; Induction period; Olefin effect

1. Introduction

Because of environmental regulation restrictions on the concentration of aromatics in gasoline, focus has shifted to increasing the concentration of other high-octane species, such as branched alkanes. Linear alkane isomerization is an important reaction in achieving this. Typically, Pt/chlorinated alumina is used to carry out these reactions commercially [1], but its use causes corrosion problems due to the need for continuous chlorine addition. New catalysts have been sought that do not require chlorine addition, including solid acid catalysts. Zeolites were studied initially, but these require high temperatures for reasonable activity [2,3].

To date, modified zirconias have drawn much attention because of their high acidity. Sulfated zirconia (SZ) has been widely studied for *n*-butane isomerization due to its high catalytic activity and selectivity at low temperatures [4–6]. However, rapid deactivation of SZ by coke deposition [7–9] and by reduction or loss of sulfur [10] has been a major barrier to commercial use. Nevertheless, SZ still generates great interest. A focus has been on developing a better understanding of the nature of the active sites of SZ and the reaction mechanism, thereby permitting the design of an even better catalyst.

Two hypothesized mechanisms for *n*-butane isomerization are still a subject of discussion: monomolecular pathways versus bimolecular pathways. Garin et al. [11] and Chao et al. [3] have suggested that the reaction is carried out through a monomolecular pathway in the presence of hydrogen on SZ with and without Pt promotion at 250 and 300 °C, respectively. But in contrast, most evidence in the literature, including isotopic tracing experiments, supports the idea that *n*-butane isomerization proceeds via a bimolecular pathway

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at both low and high temperatures [7,12–15]. A bimolecular mechanism involves the formation of C_8^+ cations by dimerization of two C_4 species (a secondary carbocation and butene). After rearrangement and β-scission of C_8^+ intermediates, isobutane and disproportionation byproducts are formed. In addition, this bimolecular pathway is strongly supported by the effect of butene on the reaction rate. For instance, having butene as an impurity in the feed stream appears to increase the initial rate of isobutane formation and catalyst deactivation [16–21]. Many studies on the effect of introducing butene to the reaction at various temperatures have shown that butene indeed promotes catalyst activity [16,17,19,20]; however, the positive impact of butene addition is offset by an increased deactivation rate due to increased coke/oligomer formation.

But is butene the only olefin capable of enhancing the overall catalytic activity of SZ? What is the effect on catalyst activity and selectivity if propylene or 1-pentene is added to the reaction? To answer these questions, we investigate the effect of propylene and 1-pentene addition on the SZ activity and compare it with the effect of 1-butene addition. The addition of three different types of olefin to n-butane isomerization may permit a better understanding of the nature of active sites developed during the induction period.

2. Experimental

2.1. Catalyst preparation and characterization

The sulfate-doped zirconium hydroxide [$Zr(OH)_4$] precursor (X20 1249/01; MEI, Flemington, NJ) was calcined at 600 °C under static air for 2 h, then cooled to room temperature over a 4-h period. The sulfur content of the calcined SZ was measured by Galbraith Laboratories, Knoxville, TN. The BET surface area of the SZ catalyst was determined by N_2 adsorption using a Micromeritics ASAP2010 (Norcross, GA). The crystallinity of the calcined catalyst was determined using a Philips X'Pert X-ray diffractometer with monochromatized Cu-K_α radiation and a Ni filter, operated at 40 kV and 30 mA.

2.2. n-Butane isomerization

The reaction was carried out in a differential quartz microreactor with an inner diameter of 8 mm. The maximum reaction conversion was $<10\%$, to minimize temperature and concentration gradients. A thermocouple was placed in the reactor touching the catalyst bed. The calcined SZ catalyst (0.2 g) was carefully placed on a porous frit inside the reactor to obtain a uniform catalyst bed, then covered with quartz wool. The catalyst was pretreated in situ at 315 °C for 4 h (with the temperature ramped at 2 °C/min and held constant at 100 °C for 1 h before heating to 315 °C) under 30 cc/min of dry, hydrocarbon-free air (National Specialty Gases, Zero Grade) before reaction. The catalyst was cooled to the reaction temperature of 100 or 150 °C under air and flushed with 30 cc/min of He (National Specialty Gases, UHP) for 30 min before the reactant stream was introduced. The reaction pressure was kept constant at 1.5 atm to connect this work to future studies with the use of SSITKA.

A reactant stream containing 5% n-butane + 1% Ar in a balance of He (Hollox, UHP) was diluted by a stream of pure He to obtain a partial pressure of n-butane equal to 0.037 atm. The total flow rate was kept constant at 60 cc/min (STP). The small concentration of olefin impurities present in the n-butane stream was removed using an H-mordenite trap held at room temperature. No olefins were detectable by gas chromatography after the trap. The alkane impurities contained in the n-butane feed to the reactor were 70 ppm isobutane, 12 ppm isopentane, and 2 ppm n-pentane. In the case where olefin (1% propylene/He, Liquid Technology; 1% 1-butene/He, National Specialty Gases; or 1% 1-pentene/He, Matheson Tri-Gas) was added, the flow of pure He was adjusted to maintain a constant flow rate of n-butane. The gas space velocity was 24,000 h^{-1}. The reactant inlet line before the reactor was heated with heating tapes to 100 °C to minimize the adsorption of added olefin on the stainless steel.

The effluent samples were analyzed using a Varian 3700 gas chromatograph (GC) equipped with a 12-ft 15% Squalane CP-AW-DMCS/Chromosorb 80/100-mesh column with a flame ionization detector. The GC oven was held at 35 °C for 14 min and then ramped to 70 °C at 10 °C/min. Byproducts were identified using a known standard gas mixture. The reaction was started by replacing a He purge stream with the reactant stream, which took about 15 s to reach the catalyst bed, followed by another 20 s for the product and reactant effluent to reach the sampling valve. To follow reaction progress during the induction period, 16 samples were collected with time-on-stream (TOS) using a 34-port VICI autosampling valve. All experiments were reproducible within a maximum error of ±5%.

3. Results

3.1. Catalyst characterization

The sulfur content and the BET surface area of the calcined SZ were measured as 1.7 wt% and 137 m^2/g, respectively. X-Ray diffractometry analysis showed that ZrO_2 was in the tetragonal phase. No other crystalline phases were detected.

3.2. Effect of olefin addition on activity

An earlier study in our lab [22] found no heat and mass transfer limitations for n-butane isomerization on SZ between 130 and 170 °C in the reaction conditions used here. Therefore, the reaction kinetic rates at 100 and 150 °C are certainly not limited by those effects either. To more precisely characterize the impact of olefin concentration on the induction period, we conducted experiments primarily at the relatively low reaction temperature of 100 °C, to lengthen the induction period and reduce catalyst deactivation. Most results at 100 °C are shown only for the first 40 min TOS, to emphasize what occurs during the induction period. (Although the reaction was studied for 100 min TOS, little additional information was ascertained from the results for 40–100 min.) The first reaction data point was taken with a fully established flow of the reactant stream.

Fig. 1 illustrates the effect of continuous addition of the different types of olefin (propylene, 1-butene, and 1-pentene) with varying O/P ratios on the formation rate of isobutane at 100 °C. We can see that not only 1-butene, but also propylene and 1-pentene, enhanced catalyst activity. The isobutane formation rate increased and the induction period decreased with increasing olefin concentration. Due to a combination of activity and deactivation effects, the optimum maximum catalyst activity was observed at molar ratios of 0.009 for propylene and 1-pentene addition and 0.012 for 1-butene addition. Increasing the olefin concentration beyond this value only accelerated catalyst deactivation and decreased isobutane selectivity (not shown). As expected, the use of olefins, which are good coke precursors, also resulted in increased catalyst deactivation with TOS with increasing concentrations added. Fig. 1 also shows that at very low concentrations, propylene had the greatest affect on accelerating the reaction rate, followed by 1-pentene and then by 1-butene. But the effects of these three olefins on reaction rates at the optimum concentrations were essentially similar, resulting in similar absolute maxima in rate of isobutane formation (around 0.16 μmol/(g$_{cat}$ s)) (Fig. 2a). Only small differences in catalyst deactivation were observed for the different olefin additions.

To obtain a better understanding of the effect of olefin addition on the induction period, we introduced propylene, 1-butene, and 1-pentene to the feed stream at 100 °C for only the first 2 min of reaction at the optimum O/P ratio determined from earlier experiments. The results (Fig. 2b) show that higher activities (around 0.13 μmol/(g$_{cat}$ s)) and shorter induction periods (around 10 min) compared with no olefin addition were still obtained even though the olefin flows were terminated after only 2 min TOS. Adding olefin for 2 min initially enhanced catalyst activity similarly for every olefin that we studied.

Table 1 compares catalyst deactivation as a result of olefin addition, determined by calculating the deactivation rate constants (k_d). Unsurprisingly, k_d increased as the concentration of olefin continuously added to the reaction increased. We also found that k_d increased in the order of 1-C$_5^=$ < 1-C$_4^=$ < C$_3^=$. The deactivation constants for the 2-min olefin additions were slightly higher than those for no olefin addition, as was expected because of the higher maximum rates; however, they were all identical for the various olefins.

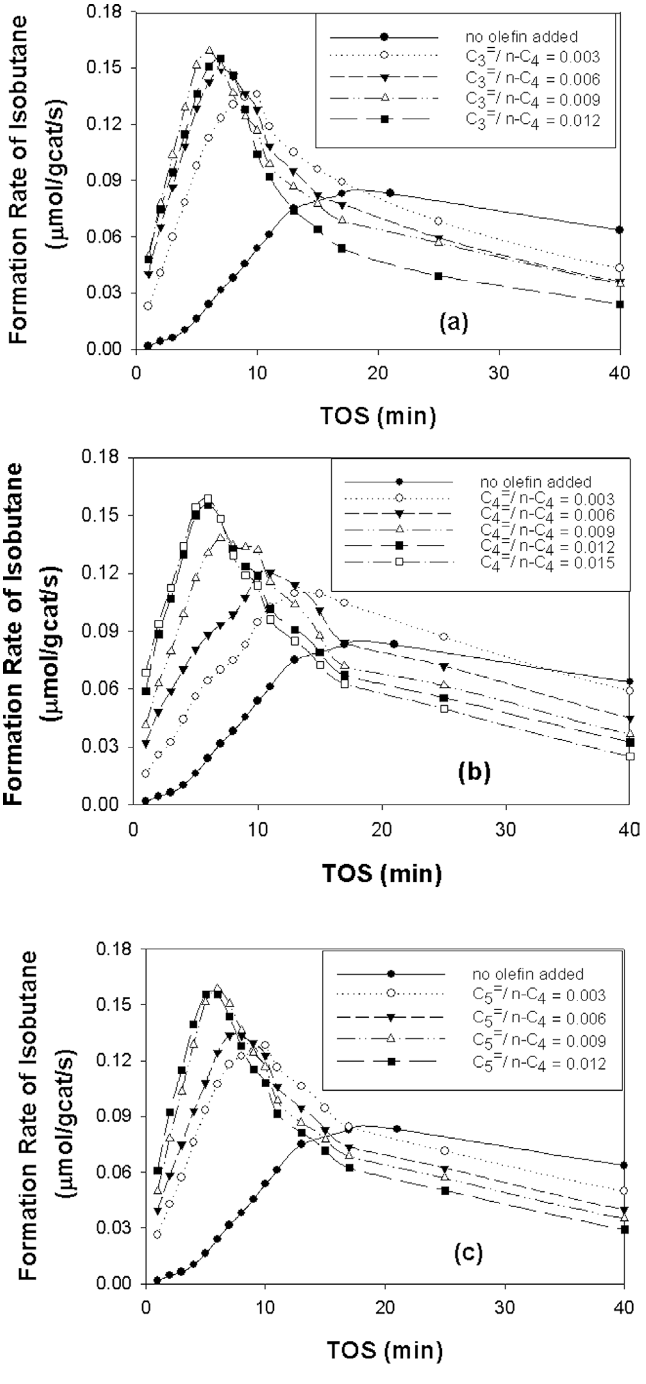

Fig. 1. The reaction rate at 100 °C in the absence and for continuous addition of (a) propylene, (b) 1-butene, and (c) 1-pentene.

We also studied the effect of adding the three olefins on the induction period at 150 °C to ensure that the effect of the olefins on catalytic activity is not temperature dependent. Propylene, 1-butene, and 1-pentene were fed continuously and for 2 min initially to the reaction at 150 °C; the results are shown in Figs. 3a and b, respectively. Because of more rapid catalyst deactivation at higher temperatures, the catalyst was exposed to added olefins only at the O/P ratio of 0.003. Similar to the reaction at 100 °C for both continuous

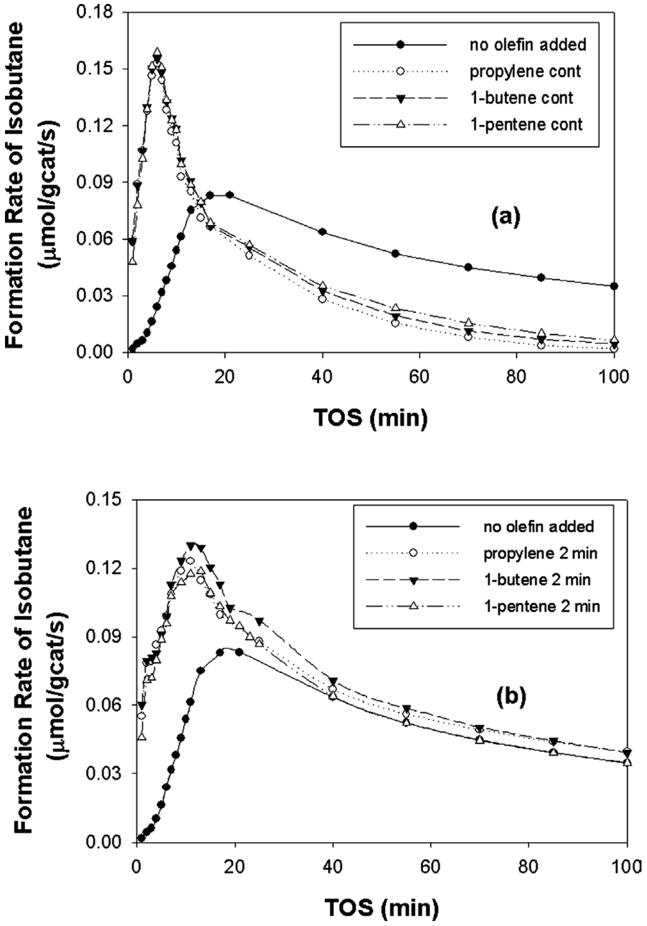

Fig. 2. The reaction rate at 100 °C when propylene, 1-butene or 1-pentene was added at the optimum O/P ratio (O/P ratio = 0.009 for $C_3^=$ and 1-$C_5^=$, and 0.012 for $C_4^=$) (a) continuously and (b) during only the initial 2 min of reaction.

Table 1
Deactivation rate constants[a] [k_d (min^{-1})] for n-butane isomerization during the absence or addition of various olefins at 100 °C

Olefin	Olefin/paraffin ratio						
	2 min addition, optimum ratio[b]	Continuous addition					
		0	0.003	0.006	0.009	0.012	0.015
None	–	0.010	–	–	–	–	–
Propylene	0.013	–	0.027	0.032	0.045	0.051	–
1-Butene	0.013	–	0.018	0.037	0.041	0.044	0.052
1-Pentene	0.013	–	0.020	0.028	0.032	0.040	–

[a] The deactivation rate constant (k_d), defined by $r_{iso}(t) = r_o \exp(-k_d t)$ after the induction period, where $r_{iso}(t)$ is the rate of n-butane isomerization and r_o is the maximum rate after the induction period. Max error = ±0.0007 min^{-1}.

[b] The optimum ratios for propylene, 1-butene, and 1-pentene were 0.009, 0.012, and 0.009, respectively.

and initial 2 min additions, the catalytic activity for SZ was also sped up by olefin addition, regardless of the olefin type used (Fig. 3). The addition of olefin for the first 2 min of reaction caused a long-term positive effect on catalyst activity for SZ lasting longer than 250 min TOS. This resulted in better catalyst activity than was seen with no olefin addition.

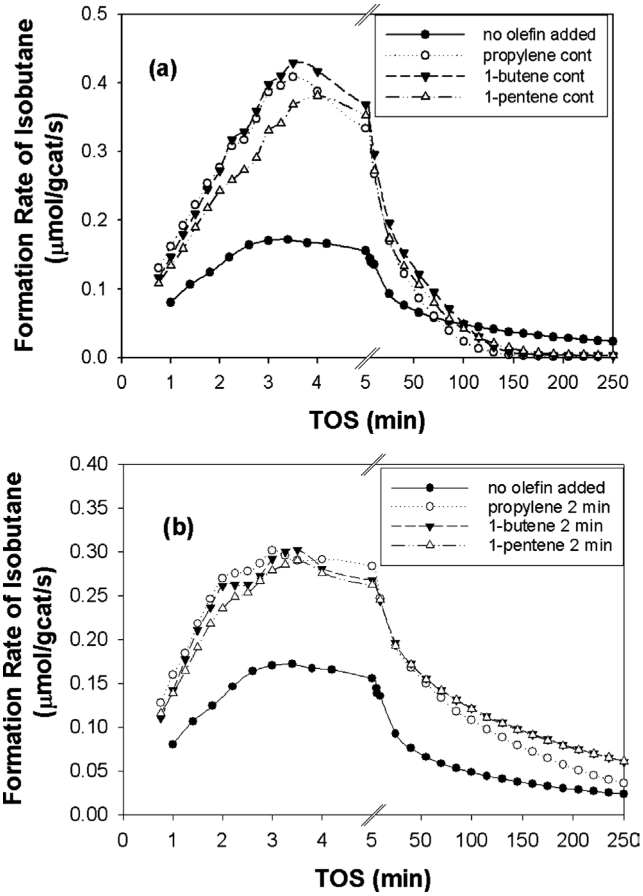

Fig. 3. The reaction rate at 150 °C when propylene, 1-butene or 1-pentene was added at the O/P ratio = 0.003 (a) continuously and (b) during only the initial 2 min of reaction.

Likewise, continuous propylene addition resulted in a somewhat higher deactivation rate constant (0.03 min^{-1}) than that for 1-butene addition (0.026 min^{-1}) and 1-pentene addition (0.022 min^{-1}).

3.3. TOS behavior of selectivity

Fig. 4 shows the variations in isobutane selectivity at 100 °C for the optimum ratios of the olefins added both continuously and during the initial 2 min of reaction. Only a nonsignificant change in isobutane selectivity with TOS was observed when no olefin was added (100 to 98%). Interestingly, when olefin was introduced during the first 2 min of reaction, isobutane selectivity increased after the olefin flow was terminated and remained stable at around 98%, regardless of the olefin added. In contrast, isobutane selectivities for the continuous addition of all olefins decreased with TOS and depended on the type of olefin added. The decrease for 100 min TOS was greater in 1-pentene (85 to 28%) than in 1-butene (93 to 39%) or propylene (93 to 78%). Propane and isopentane were the main byproducts in the absence of added olefins or when olefins were added during the initial 2 min of reaction.

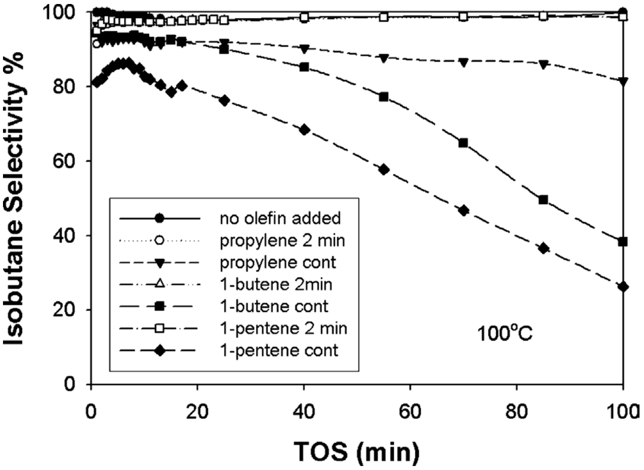

Fig. 4. The isobutane selectivity at 100 °C when propylene, 1-butene or 1-pentene was added during the first 2 min and continuously at the optimum O/P ratio (O/P ratio = 0.009 for $C_3^=$ and 1-$C_5^=$, and 0.012 for $C_4^=$).

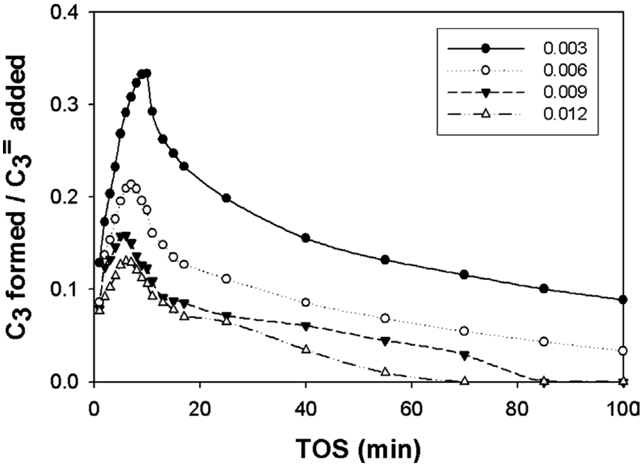

Fig. 5. The ratio of propane formed to propylene added continuously at various O/P ratios.

4. Discussion

The present study supports a hypothesized bimolecular mechanism in which butene plays a major role in this reaction, as either a part of or an aid to the production of reaction intermediates. But the results also show that not only butene, but also propylene and 1-pentene, can induce similar effects on catalyst activity during either continuous or initial 2-min additions at both 100 and 150 °C.

Li et al. [23] have suggested that isobutane is formed by the skeletal isomerization of *sec*- to *tert*-C_4^+ intermediates where the *sec*-butyl ion is produced by a protonation of butene. This suggests that a monomolecular pathway is predominant. But if hydride transfer played a significant role in producing isobutane without oligomerization, then we should observe a large amount of alkane coming out with the same number of carbons as the added olefin. However, as Fig. 5 shows, the ratio of C_3 produced to $C_3^=$ added was $<1/3$ at an O/P ratio of 0.003, and decreased with increasing added propylene concentration. Moreover, an increased rate of isobutane formation and relatively high isobutane selectivity with approximately the same value as in the absence of added olefin were observed for all TOS in the experiments of propylene addition during the first 2 min of reaction. This suggests that propylene must have participated in the formation of isobutane through oligomerization with n-butane.

The size of the oligomer chains before β-cleavage appears to be a critical factor in this reaction. The cracking of longer oligomeric chains tends to produce a wider variety of byproducts and thus less selectivity for isobutane. At similar n-butane conversion rates, continuous propylene addition produced the highest isobutane selectivity, followed by 1-butene and then 1-pentene. These results suggest that C_8^+ intermediate species (part of the originally hypothesized reaction pathway) are not the only oligomeric species yielding isobutane; the reaction must be able to proceed through the formation of C_7^+ ($C_3^= + n$-C_4) and C_9^+ ($C_5^= + n$-C_4) oligomers as well. The formation of long oligomeric chains has also been discussed by Dumesic et al. [24], who found that oligomerization of C_3–C_5 olefins with butyl ions is possible for isobutane isomerization reaction on USY zeolite.

Hammache and Goodwin [16] proposed, based in part on the long-term rate enhancement achieved by the addition of 1-butene during only the first 2 min of reaction, that butene participates in the reaction through adsorption on surface sites to form “olefin-modified sites.” Our present results suggest that not only 1-butene, but also propylene and 1-pentene, can give rise to such “olefin-modified active sites.” This implies that organic (hydrocarbon)–inorganic (SZ) sites are needed to carry out the reaction, probably regardless of whether the organic part contains larger or smaller numbers of carbon atoms.

The greater effect of propylene addition compared with 1-butene and 1-pentene addition on catalyst activity at lower concentrations seems to correlate well with the ratio of unsaturated to saturated carbon-carbon bonds (the higher the ratio, the faster the reaction); that is, the smaller the olefin, the greater its ability to form coke. But this property appears to significantly accelerate coke formation as well, resulting in more rapid catalyst deactivation (Table 1). The reaction with 1-pentene addition had the lowest k_d. These observations are in agreement with results of Praserthdam et al. [25] demonstrating that short-chain alkenes are more active than long-chain alkenes for coke formation.

The greater positive impact of olefin addition at 150 than at 100 °C may be due to a higher capability of surface sites at higher temperatures to utilize the olefin fed. However, the increases in the isobutane formation rate during the induction periods at both 100 and 150 °C was not just due to the conversion of added olefin to isobutane. For example, at 100 °C and for a ratio of 0.003, the flow rate of added 1-butene was just 0.015 µmol/(g_{cat} s), but the rate of isobutane formation at 5 min TOS was 0.04 µmol/(g_{cat} s) greater than in the absence of added olefin. This improvement was even more pronounced at 150 °C (around 0.2 µmol/(g_{cat} s) rate enhancement, compared with 0.015 µmol/(g_{cat} s) with olefin added).

Calculating the ratio of excess isobutane formed to olefin added is possible for the experiments using olefin addition during only the first 2 min of reaction. This ratio represents how many additional isobutane molecules were produced per added olefin molecule, because an increase in isobutane formation rate was still observed even though the flow of olefin was stopped. This ratio was calculated by integrating the area between the reaction rate with and without olefin addition for the entire reaction period (Figs. 2b and 3b). The excess amount of isobutane produced was determined from time = 0 to 100 and 250 min at 100 and 150 °C, respectively. At 100 °C, this excess amount was 102 µmol/g_{cat} when 1-butene was added at 0.06 µmol/(g_{cat} s) during the first 2 min; thus the ratio was 14, which is consistent with the value of 10 reported by Tabora and Davis [17] for the addition of *trans*-2-butene to n-butane isomerization on SZ at 50 °C. This ratio was 14 for propylene addition and 13 for 1-pentene addition. The ratios at 150 °C were 685 for propylene addition, 692 for 1-butene addition, and 690 for 1-pentene addition. This suggests approximately 692 turnovers of the olefin-modified sites, which is also in agreement with the value of 700 found by Hammache and Goodwin [16] for 1-butene addition at the same conditions. This ratio suggests an irreversible adsorption of olefin on SZ to produce long-lasting active sites for n-butane isomerization. It has also been suggested by Li et al. [26] that generated butene gives rise to multiple cycles of n-butane isomerization on SZ at 100 °C.

Coelho et al. [19] and Hammache and Goodwin [16] have concluded that the formation and accumulation of intermediates on the catalyst surface produce the induction period. They have suggested that olefinic species are formed and active sites activated during this period. Our results support the idea that the induction period does not comprise merely the time it takes to generate sufficient olefin to activate all of the active sites. For instance, when the concentration of added butene was varied from 75 to 375 ppm (equivalent to $1\text{-}C_4^{=}/n\text{-}C_4$ ratios of 0.003 to 0.015), representing much more butene than could be formed via dehydrogenation of n-butane at these reaction conditions, the reaction still proceeded through an induction period of at least 5 min. If producing butene from n-butane is normally (i.e., in the absence of olefin addition) the slowest step, then no induction period should be observed when such significant quantities of butene are added to the reaction.

5. Conclusions

We were able to enhance SZ activity during n-butane isomerization by adding 1-butene, propylene, or 1-pentene at both 100 and 150 °C. The continuous addition of these three olefins enhanced isobutane formation and catalyst deactivation in similar manners. Isobutane selectivity with olefin addition decreased with TOS and olefin concentration and varied with the type of olefin added. The induction period decreased and the maximum reaction rate increased with increasing concentrations of added olefin.

The effects of nonspecific olefin addition were greatest with the olefin added for only the first 2 min of the reaction. This technique produced better catalyst activity with less negative effects on catalyst deactivation and isobutane selectivity. Adding olefin for only the first 2 min of reaction allowed us to calculate the ratio of excess isobutane molecules per olefin molecule added produced during 100 min TOS. These values were approximately 14 at 100 °C and 692 at 150 °C for the addition of all three olefins, in agreement with results reported in the literature. This suggests the participation of olefins at SZ sites to form “nonspecific olefin-modified active sites.” The increased rate of isobutane formation triggered by the three olefins suggests that other intermediates besides C_8^+ are capable of performing the reaction on SZ. Thus, based on the results of this study, we conclude that n-butane isomerization can occur through a mechanism involving other olefins besides butene.

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