On the mechanism of *n*-butane disproportionation over platinum supported on tungstated zirconia: Isotopic labeling studies

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Abstract

The reactions of *n*-butane over platinum supported on tungstated zirconia in the presence of hydrogen were studied using isotopically labeled *n*-butanes and deuterium. All reaction pathways experience isotopic effects when the hydrogen flow is replaced by an equal flow of deuterium. The non-rate-limiting formation of a bimolecular intermediate appears to account for the disproportionation products. Mass spectrometric analysis of the product stream also reveals that the intramolecular 1–2 shift of the labeled primary carbon atoms is easily detected under primary-product-only reaction regimes.

Keywords: n-Butane labeling; Disproportionation mechanism; Isotopic effect; Tungstated zirconia

1. Introduction

Since the SO_4^{2-} function in sulfated zirconia is subjected to losses upon calcination and reduction and poisons the metal function under reducing atmospheres [1,2], it appears interesting to develop zirconia-based solid acid systems promoted by oxoanions with less tendency to decompose under thermal and gaseous treatments [3–5]. In particular, tungstated zirconia [6] promoted by Pt [3–5] is a good candidate for the isomerization of alkanes heavier than C_4. The reason is that the activity of tungstated zirconia for alkane isomerization is lower than that of SO_4^{2-}/ZrO_2, but the use of the former may be justified when the equilibrium conversion toward branched isomers is large in the 500–650 K range. Nevertheless, *n*-butane can still be employed as model hydrocarbon and in this paper, we present results relevant to the mechanistic aspects of the *n*-butane reactions over Pt supported on tungstated zirconia (PtWZ), using labeled *n*-butanes and H/D exchange as the chemical probes. Sachtler et al. [7] and Rezgui and Gates [8] have suggested that a bimolecular mechanism is responsible for the isomerization and disproportionation pathways of the *n*-butane reactions over sulfated zirconia promoted with iron and manganese. From a fundamental viewpoint, it seemed interesting to us to determine whether such observations could be extended to the PtWZ system. We have chosen to monitor the formation of labeled species in a once-through configuration at low

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conversions because this may in principle shed some light on the nature of primary products formation. This is expected to be more informative than the exhaustive scrambling typically observed at high conversions. The characterization of the catalysts has been discussed elsewhere [4,5].

2. Experimental

The catalyst preparation technique has been described in detail [4,5]. In brief, hydrous zirconia obtained by precipitation with ammonia from zirconyl salts was first impregnated with a solution of ammonium metatungstate and then with aqueous hexachloroplatinic acid. This catalyst precursor (1.2 wt% Pt, 6–12 wt% WO_3) was calcined at 1096 K for one hour, followed by hydrogen reduction at 623 K for another hour. Such a procedure results in relatively low dispersion catalysts (CO/Pt = 0.10–0.12) but good n-butane isomerization selectivities [5]. Impregnation of a precalcinated (1096 K) tungstated zirconia sample with $Pt(acac)_2$ followed by a second calcination at 773 K rendered a catalyst with a higher dispersion (CO/Pt = 0.30) after reduction, but also with a much higher hydrogenolysis (C_1–C_3) selectivity [5]. Since a higher surface area of Pt implied more all-metal-catalyzed hydrogenolysis (undesirable feature from a practical viewpoint), we decided to perform our isotopic labeling studies over the catalyst obtained by co-calcination of the W and Pt precursors. The issue of how the different preparation variables affect the oxidation state of tungsten has been the subject of another publication [4] and will not be discussed here in the interest of brevity.

Pulse experiments using 99 + % certified purity $CH_3-(CH_2)_2-^{13}CH_3$ (1^*C_4) and $^{13}CH_3-(CH_2)_2-^{13}CH_3$ ($1-4^*C_4$) from Isotec were carried out using mass spectrometric detection. In addition, the steady state conversion of n-butane at $T = 573$ K in a packed bed, atmospheric reactor ($H_2:nC_4$ ratio of 0.66) was perturbed by replacing the hydrogen flow by an equal flow of deuterium (99% + from Matheson). In both pulse and flow experiments, we used a quartz U-tube packed bed reactor configuration consisting of 0.25 g of catalyst in the form of 20–45 mesh particles preceded by quartz beads as the preheating bed. The samples were activated in situ prior to reaction and analyses of products were conducted on-line using either mass spectrometric (MKS Residual Gas analyzer) or GC (HP 5880A, methyl silicone capillary column from HP, FID) detection. The description of the mass-flow and temperature-controlled stainless steel reaction system is provided elsewhere [9].

3. Results

Table 1 shows the conversion of a 0.8 ml pulse of n-butane at 623 K (99 + % Matheson) under the He/H_2 stream (15 and 10 cm^3/min, respectively) used for MS analysis. These conditions were chosen to provide a good MS signal while still keeping the occurrence of secondary products to a minimum.

Table 2 shows the peak heights of the MS signals relative to the reactant molecular ion. The small amount of double labeling from pure 1^*C_4 (see for example, doubly labeled propane and C_4), and the small extent of triply labeled propane and C_4 found when a $1-4^*C_4$ feed was

Table 1
Product composition (pulse) for the reaction of n-butane in the presence of H_2

	CH_4	C_2H_6	C_3H_8	i-C_4H_8	i-C_4H_{10}	i-C_5H_{12}	n-C_5H_{12}
Product (%)	0.27	0.29	0.89	0.10	7.13	0.48	0.24

Table 2
Relative peak height intensities for the different MS signals of multiply labeled species. The M symbol represents masses 59 (for 1^*C_4 as reactant) or 60 (for $1\text{-}4^*C_4$)

Reactant	$^*C_3^*/M$	$^*C_3^{**}/M$	$^*C_4^*/M$	$^*C_4^{**}/M$	$^{**}C_4^{**}/M$	$^*C_5^*/M$	$^*C_5^*/M$	$^{**}C_5^{**}/M$
1^*C_4	0.040	0	0.035	0	0	0	0	0
$1\text{-}4^*C_4$	0.700	0.021	n/a	0.021	0	0.024	0	0

used, are consistent with the natural abundance of ^{13}C. It is known that the natural $M + 1/M$ ratio in nC_4 is 0.044, and if we now 'block' one and two carbon atoms via isotopic labeling, the predicted $M + 1/M$ ratios would be 0.033 and 0.022 for 1^*C_4 and $1\text{-}4^*C_4$, respectively. These figures are in very good agreement with the data in Table 2, which suggests that higher order labeling was not due to reaction. No multiply labeled pentanes are detected with 1^*C_4 as reactant, whereas doubly labeled pentane is easily detected upon reaction of $1\text{-}4^*C_4$. In addition, the doubly labeled propane signal resulting from injection of $1\text{-}4^*C_4$ is markedly large. It must be realized that even if this doubly labeled molecular ion signal were due to a convolution of production of such a propane form in the reactor, intramolecular scrambling and fragmentation of doubly labeled pentanes or

butanes by the MS electron beam, the main point would still be that $m = 46$ implies that the two labels are now separated by a maximum of one carbon atom after reaction. The doubly labeled disproportionation products from $1\text{-}4^*C_4$ are expected to be primary products under the experimental conditions employed here.

Our observations are best summarized in Figs. 1 and 2, where it is evident that certain signals must be scaled up by a factor of ten to become detectable, while others are essentially zero, within experimental error. After injection of a total of eight pulses the catalyst showed no deactivation, a fact that enabled us to confirm our results by injecting the two types of labeled n-butane sequentially for a number of times over the same bed.

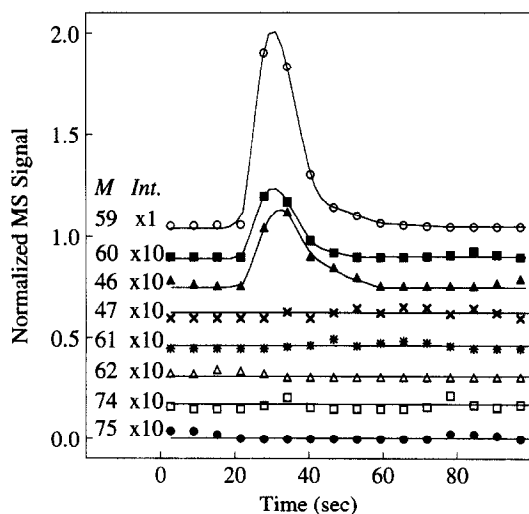When conversion was stabilized under the reacting mixture for more than two hours, the

Fig. 1. Intensity versus time curves for the reaction of a 0.8 ml pulse of 1^*C_4 over PtWZ. The intensities are normalized to the height of the $M = 59$ peak.
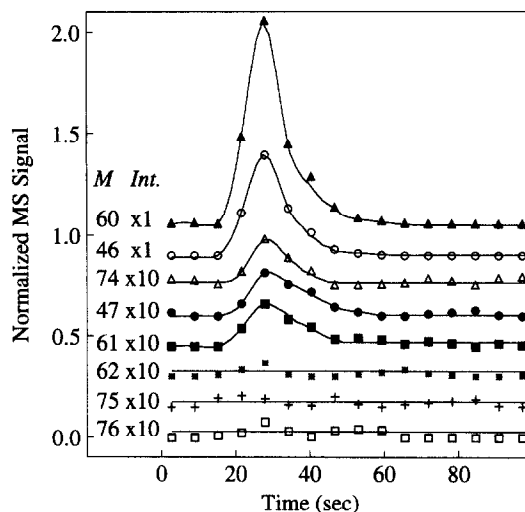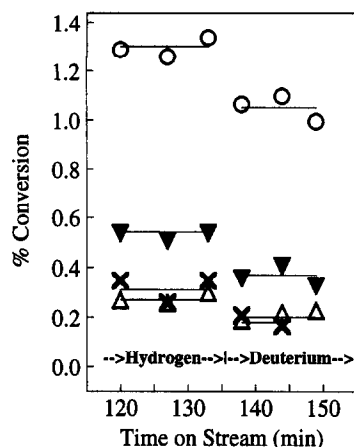

Fig. 2. Intensity versus time curves for the reaction of a 0.8 ml pulse of $1\text{-}4^*C_4$ over PtWZ. The intensities are normalized to the height of the $M = 60$ peak.

Fig. 3. Effect of H_2/D_2 switching on product formation. (○) isobutane, (▲) propane ×10, (X) 2-methylbutane ×10, and (△) methane ×10.

hydrogen flow was replaced by an equal flow of deuterium by means of a three-way valve. It was observed that hydrogenolysis, isomerization and disproportionation products all experience deuterium isotopic effects (Fig. 3).

4. Discussion

Fig. 3 indicates that the hydride abstraction steps play an important role in the overall reaction rate. The formation of doubly labeled disproportionation species upon reaction of the $1\text{-}4^*C_4$ pulse over PtWZ calls for the proposal of a bimolecular intermediate, but this is not expected to be rate-limiting. We have recently reported a reaction order in n-butane slightly below one for this reaction on PtWZ [5] (as well as a negative hydrogen dependence), an observation that is consistent with this picture. On the other hand, the hydrogenolysis products show variable reaction orders (from 0 to 1 for hydrogen) and are believed to be formed primarily on Pt sites [5]. Here, we will limit our discussion to the different mechanistic possibilities to explain the exclusive formation of doubly labeled disproportionation species at low conversions (again, note that with both 1^*C_4 and $1\text{-}4^*C_4$,

higher order labeling is explained by the natural ^{13}C abundance).

The formation of doubly-labeled pentanes from $1\text{-}4^*C_4$ is consistent with the proposal of a dimeric C_8^+ surface intermediate. However, the very large amount of doubly labeled propane molecular ions ($M = 46$) from $1\text{-}4^*C_4$ cannot be exclusively attributed to such an intermediate. In the 50–70 V ionization potential range (we operated our mass spectrometer at 70 V), the mass spectra of n-butane and isobutane have $C_3H_8^+/C_4H_{10}^+$ relative intensities of 0.27 and 1.21, respectively (see for example [10]). A simple calculation using the 7% isobutane produced during reaction of the pulse (see Table 1) shows that disproportionation alone does not account for the very high $^{**}C_3H_8^+/^{**}C_4H_{10}^+$ ratio observed. In addition, the 0.89% propane in products does not explain this figure either. The $C_3H_7^+$ peak is the dominant signal for C_{3-5} alkanes. Thus, we have turned our attention to the work of Brouwer [11] and recently to that of Sachtler et al. [12] on sulfated zirconia catalysts to explain this observation. Brouwer [11] showed that the 1–2 shift of the label depicted in Fig. 4 via a protonated cyclic carbocation is a process roughly as fast as the isomerization of n-pentane to isopentane. Therefore, it appears that the amount of $^{**}C_3H_8^+$ is also affected by the intramolecular 1–2 label shift mechanism. Interestingly, such an intramolecular rearrangement of the label was also observed for $1\text{-}4^*C_4$ over sulfated zirconia [12]. This seems to suggest that this family of oxoanion promoted zirconia catalysts are likely to differ in their intrinsic activities for alkane isomerization, rather than in the way by which this reaction is catalyzed at molecular level.

Our next step was to recognize that there are a number of possibilities from the open dimeric intermediates proposed for the classical alkane
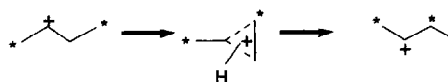

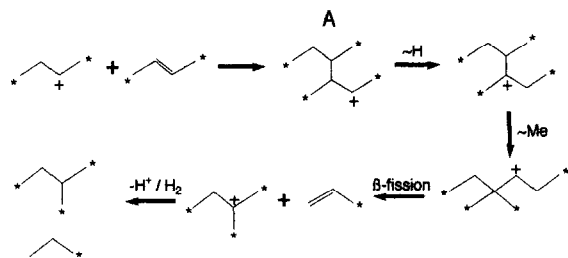Fig. 4. Cyclic carbocation intermediate for 1–2 label shift [11,12].

Fig. 5. Frustrated reaction scheme 1.

Fig. 7. Pines' cyclization mechanism.

disproportionation mechanism [13]. Figs. 5 and 6 show just two frustrated reaction pathways that would have led to triply and singly labeled disproportionation products. The first one (Fig. 5) would involve an 'up-hill' step consisting of a methyl shift to sacrifice a tertiary carbenium ion to form a secondary cation. The second scheme (Fig. 6) has both reaction channels leading to the formation of primary carbenium ions (which is energetically unacceptable), as others that we tried to generate from the B octyl cation. In addition, such a C_8^+ ion would be formed from 1-butene, which we expect to be less abundant than the 2-butenes on the catalyst surface. We have also explored a number of alternative mechanisms involving cyclizations. For example, on trying to propose a cyclic intermediate for both disproportionation and isomerization, we have considered the olefin 'conjunct polymerization' mechanism proposed
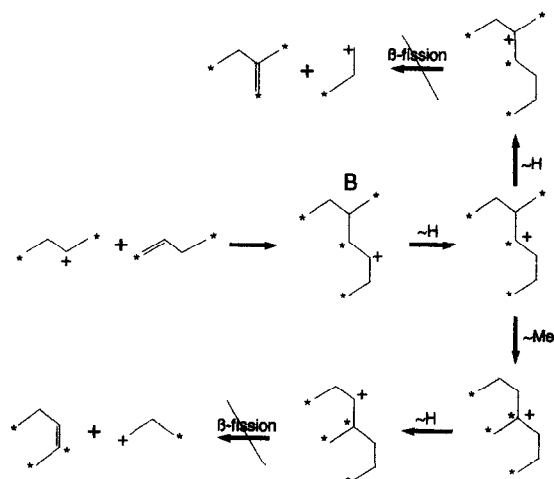

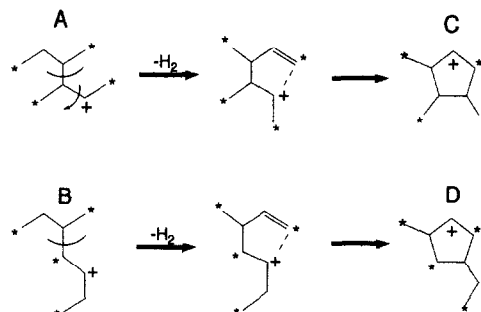Fig. 6. Frustrated reaction scheme 2.

by Pines [14]. It is well-known that naphthenic rings are precursors for solid acid catalyst deactivation, and an intramolecular cyclization mechanism has been proposed for the formation of such rings [14]. In this scenario, intermediates A and B would in principle be able to undergo cyclization if the appropriate double bond of the octyl cation becomes dehydrogenated, i.e., if the Pt and the acid function are in close proximity (Fig. 7). Once cycles C and D are formed, it is easy to show that the simplest sequences consisting of one intramolecular rearrangement (either a methyl or a hydride shift) followed by ß-ring opening and ß-fission, should have led to larger amounts of doubly labeled species from 1^*C_4 than those observed in this study. Smaller cyclic structures prior to the methyl and hydride shift steps could be invoked but we expect them to be of higher energy than those shown in our final scheme proposed in Fig. 8. Note that in the latter, the evolution of carbenium ions all the way to the product molecules does not seem to be energetically restricted. Such a scheme has also been observed in the isomerization of n-butane over H-mordenite [15] and in this matter, the acidic function of zirconia-based systems may behave in a similar fashion. The reason such a scheme would also work for 1^*C_4 is that only secondary carbon atoms are passed from molecule to molecule, making double labeling of primary products impossible. However, it must be recognized that in order for this conclusion to hold, no octyl carbocations should form as pseudo-
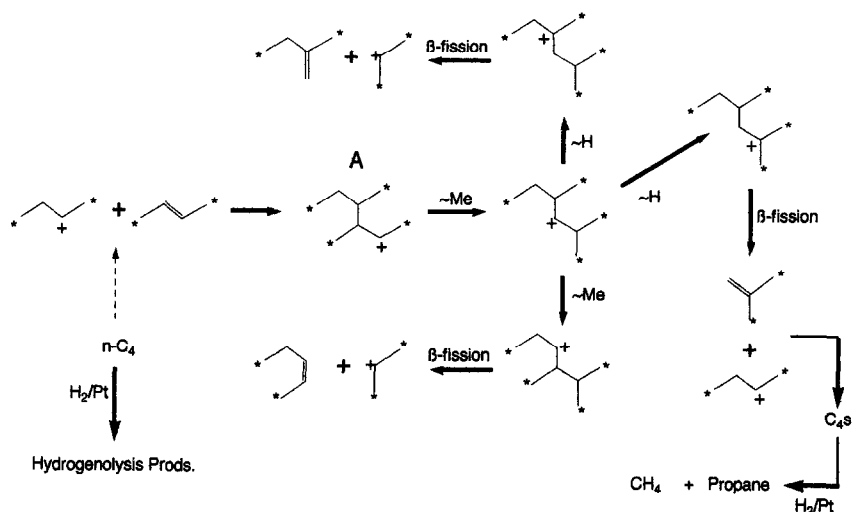
Fig. 8. Proposed mechanism.

secondary products, i.e., after a terminal carbon atom label of an n-butane molecule has shifted to an internal carbon. Therefore, we expect the disproportionation and the 1–2 label shift processes to be kinetically comparable at low conversions.

In summary, an open octyl cation bimolecular intermediate is proposed to take place when n-butane is reacted in the presence of hydrogen over platinum supported on tungstated zirconia catalysts. An intramolecular mechanism consisting of a 1–2 shift of the label in 1-4 doubly labeled n-butane appears to be responsible for the large production of doubly labeled propane in the product stream.

Acknowledgements

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