On the problems of the mechanism of the skeletal isomerization of *n*-butene

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Two different catalysts of gamma alumina and reduced tungsten oxide were studied in the reactions of *n*-butene, butyl chlorides and *n*-butanol at 350°C. It was found that the products of different butenes including isobutene, showed a similar distribution over each catalyst.

Keywords: skeletal isomerization; *n*-butene

1. Introduction

The skeletal isomerization of *n*-butene attracts an ever increasing attention in the catalytic world as some recent presentations indicate [1–3]. It is a reaction very interesting from both the fundamental and the commercial point of view.

As in other reactions, there are two main fundamental – mutually related – problems: (i) what is the mechanism of the reaction, (ii) what is the active center of the reaction. These problems are not being solved in this paper, but perhaps, our results might be of interest for people working on these problems.

In this paper two comparisons are performed:

(i) A comparison of a catalyst based on a non-transition metal oxide, the surface of which has strong Lewis acidic properties (modified gamma alumina) and of a catalyst based on a transition metal oxide (WO_{3-x}).

(ii) A comparison of the reactions of the four following molecules:

$CH_2{=}CH{-}CH_2{-}CH_3$,

$Cl{-}CH_2{-}CH_2{-}CH_2{-}CH_3$ and $Cl{-}C(CH_3)_3$,

$HO{-}CH_2{-}CH_2{-}CH_2{-}CH_3$.

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2. Experimental

Alumina based catalysts have been prepared from gamma alumina by chlorination, using various alkyl chlorides (for details see ref. [4]). Results shown below are obtained with a catalyst prepared by chlorination of alumina using various butyl chlorides. Tungsten oxide is a commercial product (Fluka, 99.9%).

Reactions were monitored in a continuous flow in all-glass apparatus working at (round) 1 bar total pressure. Standard conditions used for comparison are: 350°C, 1 bar, n-butene/$N_2 = 0.05$, total flow 20 ml/min. With butanol, saturation pressure of butanol at 20°C was applied in the feed, with butyl chlorides the saturator worked at 20°C or -15°C. This lead to a molar ratio with regard to N_2 of about 0.01 for butanol and 0.1 for butyl chlorides, respectively.

The selectivity is defined by the weight percent of each particular hydrocarbon. Results are shown in tables 1 and 2. The product distributions are shown graphically in figs. 1 and 2. It should be mentioned that unmodified gamma alumina shows an intrinsic skeletal isomerization activity but the selectivity to isobutene is always under 10%. Tungsten oxide as received is active in double bond shift of n-butene, dechlorination and dehydration of the feed but has no activity in skeletal isomerization. The latter activity appears only after a prereduction at 700°C for 1 h. There is some uncertainty in the literature with regard to the exact equilibrium concentrations but we can safely state that the double bond shift reactions and the skeletal isomerization are close to equilibrium and this state is easily achieved starting from any of the molecules tested.

Table 1

Distribution of products in the reactions of butyl chlorides, 1-butanol and n-butene at 350°C over chlorinated alumina [a]

τ (h)	Butenes				Others		
	cis-2-	n-	iso	trans-2-	$C_3(=)$	$C_5(=)$	$C_4(0)$
1-chlorobutane as feed							
0.5	19	10	35	13	7	11	5
8	25	14	40	18	1	2	0
2-chloro-tert-butane as feed							
0.5	17	8	38	11	9	11	6
7	16	8	42	12	7	10	5
1-butanol as feed							
0.5	24	14	42	17	2	0	1
5	33	17	27	23	0	0	0
n-butene as feed							
0.5	24	12	41	17	2	3	1
30	25	13	40	18	1	3	0

[a] τ: time-on-stream; $C_3(=)$ propene; $C_4(0)$ butanes; $C_5(=)$ pentenes.

Table 2
Distribution of products in the reactions of butyl chloride, butanol and *n*-butene at 350°C over reduced WO_3 [a]

τ (h)	Butenes				Others		
	cis-2-	*n*-	iso	trans-2-	$C_3(=)$	$C_5(=)$	$C_4(0)$
1-chlorobutane as feed							
0.5	40	21	9	29	1	0	1
1	43	23	4	30	0	0	0
1-butanol as feed							
0.5	41	20	11	28	0	0	0
1	43	21	6	30	0	0	0
n-butene as feed							
0.5	39	20	5	26	0	0	10
1	41	20	5	28	0	0	6

[a] Symbols as in table 1.

3. Discussion

An inspection of the data in tables 1 and 2 reveals a striking similarity between the product distributions of the three molecules studied. Since the experimental conditions applied disfavour the bimolecular mechanism, we shall confine our consideration to the monomolecular mechanism [4].

The simplest possibility is that butanol dehydrates and butyl chloride dechlorinates into *n*-butene with not only the double bond shift but also the elimination reactions (H–OH and H–Cl elimination) being faster than the skeletal isomerization.

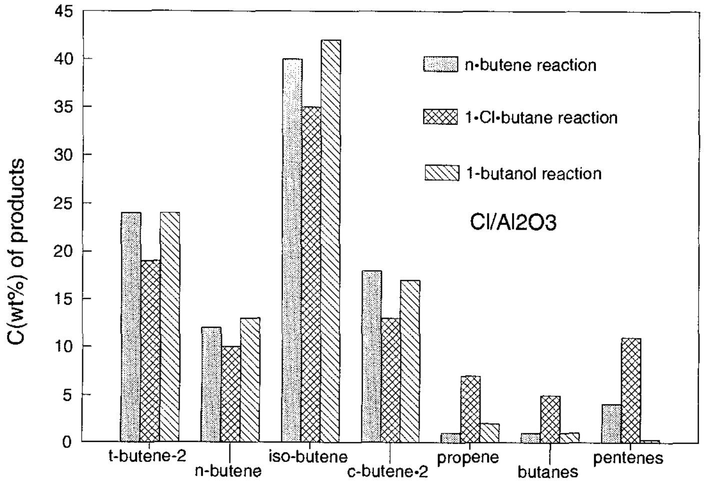


Fig. 1. Reactions of butyl chloride, butanol and *n*-butene over chlorinated alumina at 350°C.

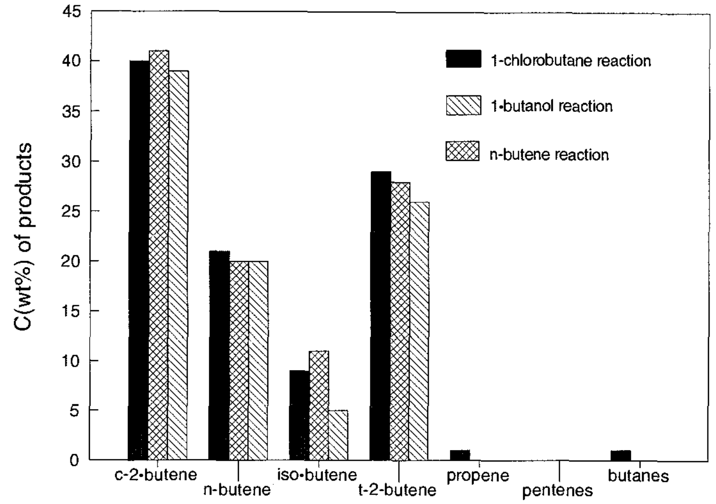


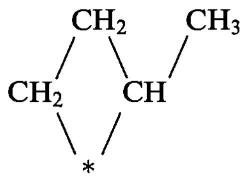
Fig. 2. Reactions of butyl chloride, butanol and *n*-butene at 350°C over reduced WO_{3-x}.

However, it is also possible – although not proven here – that the chloride and the alcohol are easily converted in the adsorbed state directly into an intermediate which can also arise from *n*-butene. A search for ideas in the literature reveals that one can consider three possibilities as being more than pure speculations:

(i) By elimination of H–Cl or H–OH and of an additional H, an adsorbed *allyl-like species* is formed, which can be an intermediate in bond shift isomerization or the skeletal isomerization [5,6].

(ii) By elimination of Cl or OH from substituted butenes or by addition of H (from a surface OH) to *n*-butene, a *butoxy species* is formed [7]. One can for example, speculate that by hydrogen shifts and CH_3 migration the isobutoxy species is formed which is converted subsequently into isobutene.

(iii) Elimination reaction on substituted butenes or adsorption of *n*-butene both lead to the formation of *metallacyclobutane* which allows $CH_2{=}*$ species to migrate along the rest of the molecule (scheme 1).



Scheme 1. Metallacyclobutane

Bolton et al. [8] collected results which can be explained as support for migration of CH_x species. According to Bolton et al. this transfer can be also inter-molecular. Derouane et al. [9] produced convincing evidence by NMR that the intra-molecular CH_x transfer is freely occurring on Ga(III) sites in zeolites. Al(III) can, perhaps, do the same.

With all three above mentioned intermediates, the skeletal isomerization would always involve a new C–C bond formation and CH_x migration. It is therefore interesting to learn how good or bad are the isomerization catalysts in C–C bond formation, starting with C_1-building units. It is well known that C_n-hydrocarbons can be formed from C_1-units, which in their turn are produced from e.g. CH_3OH on zeolites and alumina supported WO_3. The mechanism which has been recently suggested [10,11] to explain the synthesis contains elementary steps which, in principle, could be adopted for skeletal isomerization, too. Therefore, we have monitored the reaction of CH_3OH on chlorinated and fluorinated aluminas at the conditions: $CH_3OH/N_2 = 0.15$, 450°C and total flow rate 20 ml/min. It was found that about 50% CH_3OH were converted into C_2 (ethene and ethane) over chlorinated alumina and about 90% CH_3OH into C_2 (ethane and ethene) but also C_3, C_4 and C_5 hydrocarbons (essentially olefins) over fluorinated alumina. Thus, although alumina is not a good metathesis catalyst, an isomerization mechanism involving CH_x migration cannot be neglected.

We do not see a possibility to discern at this stage between the mechanisms listed. However, it is our hope that this can happen in the near future.

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