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Selective isomerization of butene to isobutene

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To identify the elements active for the skeletal isomerization of *n*-butene, a search along the periods of the periodic system has been performed. It is shown that the group VIA (Cr, Mo and W) oxides and the Al oxide are potentially active catalysts. The reaction mechanism and the nature of the active sites are also discussed in relation to the information from the literature.

Keywords: skeletal isomerization; *n*-butene; Cr, Mo, W and Al oxides

1. Introduction

There is a considerable practical interest in the selective isomerization of butene to isobutene. Refineries are facing the situation of a coming overproduction of linear butenes, while isobutene would be a very desirable raw material to make methyl tert-butyl ether (MTBE), which is an excellent octane number booster and can bring "oxygen" in the gasoline produced, as required by recently formulated new laws.

We have examined in the first paper [1] the skeletal isomerization of *n*-butene over pure (γ-) alumina and over halogenated alumina. It was proposed that *n*-butene undergoes skeletal isomerization over Lewis acid sites, possibly through a formation of π-allylic carbanion. In this paper we report the results concerning a study on the group IV, V and VIA oxides and some other oxides as catalysts for the skeletal isomerization of *n*-butene.

2. Experimental

2.1. CATALYTIC TESTING

The reaction was carried out at 350°C and atmospheric pressure in a conventional continuous flow gas fixed-bed reactor, previously described [1]. Samples of 1 g (0.3 g in few cases: Re_2O_7 and MoO_3/SiO_2) were reduced in situ at the temperatures within the 350–700°C range under hydrogen flow (20 ml/min), and then a flow of 5% *n*-butene diluted in hydrogen (or nitrogen) was lead over the catalyst kept at 350°C. The gas flow rates were fixed using a Bronkhorst mass flow controller and, when required, the mixture could be saturated with additives by bubbling it through a saturator (which was kept at 20°C with water). The total flow rate was checked at the exit of the reactor by a soap film-meter. The reaction products were analyzed by gas chromatography (Hewlett Packard), equipped with a KCl/Al_2O_3 column working at 100°C, with a possibility of programmed rise in temperatures of 100°C (in 15 min) and 180°C (in 20 min).

2.2. CATALYST PREPARATION

The catalysts studied were obtained by different procedures. Most of the pure oxides used as catalysts were just the commercial products (table 1). TiO_2 and ZrO_2 were obtained from the metal chlorides by precipitation with ammonia solution. These precipitates have been washed repeatedly by ammonia solution in order to eliminate the remaining chlorine, and then dried at 120°C overnight. CaO and Re_2O_5 were prepared in situ in the reactor, under nitrogen flow, by decomposition of their salts: $CaCO_3$ at 700°C and NH_4ReO_4 at 400°C. γ-Al_2O_3 was made from boehmite of a high purity (AKZO) through calcination at 600°C in air for 6 h. This alumina was also used as a support for different other oxides.

The catalyst 0.5% $Pt/ZrO_2-SO_4^{2-}$ (table 2), known to behave as a superacid in the skeletal isomerization of *n*-butane, was prepared according to the authors [2].

The V, Cr, Mo, W, and Re oxides the results on which are shown in table 3 were prepared by impregnation using 1.5 ml solution per 1 g carrier. The nominal metal oxide loading was calculated from the concentrations of impregnation solution. The sample prepared by Na_2WO_4 impregnation, was treated first in hot concentrated nitric acid to decompose the salt and also washed to remove $NaNO_3$, all steps as described in ref. [3].

The V, Cr, Mo, W, and Re oxides the results on which are given in table 4 were made by the so-called ion-exchange method (or equilibrium adsorption), using

Table 1
The oxides investigated in the reaction of skeletal isomerization of *n*-butene at 350°C

	MgO	CaO	La_2O_3
	TiO_2	ZrO_2	
	V_2O_5	Nb_2O_5	Ta_2O_5
	Cr_2O_3	MoO_3	WO_3
	Re_2O_7	Fe_2O_3	ZnO
	γ-Al_2O_3		
	PbO_2	SnO_2	Bi_2O_5
	Nd_2O_3	Sm_2O_3	
possible activations:	(1) dehydrogenation in N_2 at 450–600°C, (2) reduction in H_2 at 350–500°C, (3) chlorination at 350°C using butylchloride		

Table 2
n-butene reactions at 350°C under standard conditions over the unsupported oxides with indicated activation at indicated time-on-stream [a]

Catalyst activation	τ (h)	C_4H_8			Byproducts	
		n-	2-	iso	$C_3^=$	C_4^0(iso)
γ-Al_2O_3	*n*-C_4H_8 diluted in N_2					
no	1–5	22	73	5	0	0
H_2/450°C/2 h	1	17	59	14	1	9(1)
C_4H_9Cl/350°C/1 h	1–30	14	42	41	1	2
MoO_3	*n*-C_4H_8 diluted in H_2					
H_2/450°C/0.5 h	0.5	0	0	0	5	95(50)
H_2O	1	16	56	9	0	19(3)
WO_3	*n*-C_4H_8 diluted in H_2					
H_2/700°C/1 h	1	21	68	5	0	6(1)
0.5% *Pt/ZrO_2–SO_4^{2-}*	*n*-C_4H_8 diluted in H_2 and then in N_2					
cal. 600°C/2 h						
H_2/350°C/2 h	1_{H_2}	9	27	9	2	53(9)
	2_{N_2}	18	63	14	2	3(1)

[a] τ: time-on-stream; *n*-: *n*-butene; 2-: 2-butenes, iso: isobutene; $C_3^=$: propene; C_4^0(iso): *n*-butane and isobutane.

250 ml solution of 0.05 M metal ion per 5 g γ-Al_2O_3. The pH value in the aqueous solution was adjusted by HNO_3 addition to be within 1.5–2, in order to obtain a sufficient quantity of adsorbed metal oxo-anions on alumina. The difference of weights before and after adsorption of metal precursors supplied an estimate of the metal oxide loadings. These values are also given in table 4.

The preparation from nonaqueous solution in a dry box was applied to the catalysts with Ti, Zr, Nb and Ta oxides on alumina, which are listed in table 5. The sample of 5 g alumina, previously dehydrated at 400°C in vacuum overnight, was put into 200 ml CCl_4 solution containing 2 g of dissolved metal chlorides. This mixture was then kept upon stirring for 6 h and filtered in a Büchner flask to remove the solvent (CCl_4) by vacuum pumping. The solids were treated by water to hydrolyze the supported metal chlorides, and further washed by ammonia solution to completely dechlorinate the catalyst. After drying at 120°C overnight, the weights of these solids were used to estimate the minimum amounts of deposited metal oxides on alumina (see table 5). One catalyst ZrO_2/Al_2O_3 (30%) was prepared by wet impregnation using the nonaqueous solution of $Zr(C_2H_5O)_2$ dissolved in water-free cyclohexane (table 5).

Two samples of Mo/SiO_2 catalyst were prepared by the so-called grafting method, with $MoCl_5$ used as precursor, and kindly prepared by the authors of this technique [4]. Their called samples were calcined in air at 600°C for 2 h. One of

Table 3
n-butene reaction at 350°C under standard conditions over the impregnated catalysts (V, Cr, Mo, W and Re oxides) at indicated time-on-stream [a]

Catalyst activation	τ (h)	C_4H_8			Byproducts		
		n-	2-	iso	$C_3^=$	C_4^0	$C_5^=$
WO_3/Al_2O_3	*n*-C_4H_8 diluted in H_2–H_2O						
5% H_2–H_2O/400°C/3 h	1	17	57	3	0	23	0
30% H_2–H_2O/400°C/3 h	1	14	47	23	4	5	7
	2	16	52	21	3	4	4
MoO_3/Al_2O_3	*n*-C_4H_8 diluted in H_2–H_2O						
2% H_2–H_2O/400°C/16 h	2	20	71	2	0	7	0
5% H_2–H_2O/400°C/16 h	3	21	71	4	0	4	0
16% H_2–H_2O/400°C/16 h	3	17	58	5	0	20	0
30% H_2–H_2O/400°C/16 h	2	17	59	6	0	18	0
Cr_2O_3/Al_2O_3	*n*-C_4H_8 diluted in H_2–H_2O						
10% H_2–H_2O/400°C/16 h	2	17	53	0	0	30	0
30% no reduction	1	25	75	0	0	0	0
30% H_2–H_2O/400°C/16 h	0.5	70% CH_4 and C_2, 30% C_4H_{10}					
Re_2O_5/Al_2O_3	*n*-C_4H_8 diluted in N_2–H_2O						
10% H_2–H_2O/400°C/16 h	0.5	90% CH_4 and C_2, 10% C_4H_{10}					
30% no reduction	2	24	73	1	1	0	1
V_2O_5/Al_2O_3	*n*-C_4H_8 diluted in H_2–H_2O						
10% H_2–H_2O/400°C/16 h	1	24	74	0	0	2	0
30% H_2–H_2O/400°C/16 h	1	53	47	0	0	0	0
MoO_3/SiO_2	*n*-C_4H_8 diluted in H_2–H_2O						
10% H_2/400°C/16 h	1	18	57	2	0	23	0
WO_3/SiO_2	*n*-C_4H_8 diluted in H_2						
30% H_2/700°C/1 h	0.5	26	70	4	0	0	0
	1	28	71	1	0	0	0

[a] C_5: pentenes and pentanes; Al_2O_3: γ-Al_2O_3; C_2: C_2H_4 and C_2H_6; other symbols as in table 2.

the samples is the unwashed one, containing molybdenum blue (about 10% MoO_3) (table 3), which should behave [4] like a polycrystalline MoO_3 catalyst. Another sample is the washed oxide, containing only grafted Mo oxide (about < 1% as MoO_3). The oxide is highly dispersed on silica and known to be catalytically different from the former one [4].

The metal salts employed in these preparations are $CaCO_3$ (Janssen Chimica, hereafter called JC, 99%), $TiCl_4$ (JC, 99.9%), $ZrCl_4$ (JC, 98%), NH_4ReO_4 (Johnson Matthey, 99.9%), $Na_2WO_4 \cdot 2H_2O$ (JC, >99%), NH_4VO_3 (JC, >98%), $Cr(NO_3)_3 \cdot 9H_2O$ (JC, 99%), $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (JC, >99%), $NbCl_5$ (JC,

Table 4
n-butene reaction at 350°C under standard conditions over the ion-exchanged catalysts (V, Cr, Mo, W and Re oxides) at indicated time-on-stream [a]

Catalyst activation	τ (h)	C_4H_8			Byproducts		
		n-	2-	iso	$C_3^=$	C_4^0	C_5
WO_3/Al_2O_3	*n*-C_4H_8 diluted in H_2–H_2O						
35% H_2–H_2O/400°C/16 h	1	11	40	22	7	9	11
	2	13	44	22	5	7	9
	5	14	51	22	2	6	5
MoO_3/Al_2O_3	*n*-C_4H_8 diluted in N_2						
12% H_2–H_2O/500°C/16 h	1	16	63	14	2	4	1
Cr_2O_3/Al_2O_3	*n*-C_4H_8 diluted in H_2						
8% H_2–H_2O/500°C/16 h	1	22	69	7	0	2	0
V_2O_5/Al_2O_3	*n*-C_4H_8 diluted in H_2–H_2O						
10% H_2–H_2O/500°C/16 h	3	23	75	2	0	0	0
Re_2O_5/Al_2O_3	*n*-C_4H_8 diluted in N_2–H_2O						
15% no reduction	1	24	73	2	1	0	0

[a] All symbols as above.

Table 5
n-butene reaction at 350°C under standard conditions over the catalysts (Ti, Zr, Nb, Ta and Mo oxides) prepared from metal chlorides, at $\tau = 1$ h [a]

Catalyst	Oxide loading	NH_3 solution (2 M) washing	C_4H_8		
			n-	2-	iso
TiO_2/Al_2O_3	>20%	no	22	72	6
		yes	23	76	1
ZrO_2/Al_2O_3	>20%	no	17	59	24
		yes	23	74	3
NbO_2/Al_2O_3	>20%	no	18	60	22
		yes	23	74	3
TaO_2/Al_2O_3	>20%	no	20	66	14
		yes	24	74	2
MoO_3/SiO_2	< 1%	H_2/400°C/15 h	60	40	0
$Zr(ETO)_2$ as precursor					
ZrO_2/Al_2O_3	30%	cal. 600°C/2 h	24	74	2

[a] *n*-butene diluted in dried nitrogen flow, other symbols as above.

99.8%), $TaCl_5$ (JC, 99.9%) and $Zr(C_2H_5O)_2$ (Alfa, 99%). The used commercial oxides are MgO (JC, >97%), La_2O_3 (JC, 99.9%), V_2O_5 (JC, 98%), Nb_2O_5 (JC, 99.9%), Ta_2O_5 (JC, 99%), Cr_2O_3 (JC, 99%), MoO_3 (JC, 99%), WO_3 (Fluka, 99.9%), Fe_2O_3 (Fluka, >98%), ZnO (JC, 99.5%), PbO_2 (JC, >97%), SnO_2 (JC, 99.9%), Bi_2O_5 (JC, 99.9%), Nd_2O_3 (JC, 99.9%) and Sm_2O_3 (JC, 99.9%).

3. Results

3.1. PURE OXIDES

When the oxides (table 1) are used without any pretreatment, only γ-Al_2O_3 is active in the skeletal isomerization of *n*-butene at 350°C (table 2). This activity (5% isobutene) is not very much influenced by the use of other carrier gases (H_2 or N_2) and by added water vapor. However, a heat- and reduction-treatment can induce the activity of various oxides and enhance that of alumina.

An appropriate "reduction" of γ-Al_2O_3 has a positive effect on the desired selectivity to isobutene (table 2). When MoO_3 was slightly reduced at 450°C in H_2 for 30 min, 95% butenes are hydrogenated into butanes and among the products there is about 50% isobutane. Such skeletal isomerization can occur after the hydrogenation [5] or before it. The most important to be noticed here is that water (saturating at 20°C the H_2 flow) sharply and quickly suppresses hydrogenation and enables the reduced MoO_3 to skeletally isomerize *n*-butene (see table 2). For WO_3, a reduction at 700°C (for 1 h) is needed to achieve the selectivity to isobutene of 5%. In contrast to the reduced MoO_3, water in the flow lowers the skeletal selectivity. The selectivities are comparable with that obtained with γ-Al_2O_3.

The thermal treatment in H_2 of other reducible metal oxides does not induce any positive effect for the skeletal isomerization of *n*-butene and mostly leads to hydrogenation or hydrogenolysis of butenes.

The chlorination effect on alumina is so strong that the desired selectivity to isobutene (40%) is close to the thermodynamic limit (43%) at 350°C. However, such effect is not achieved with the other oxides.

It should be noted here that inspite of the attempted activation, the oxides PbO_2, SnO_2 and BiO_5 were not active even for the otherwise easy double bond isomerization. Other oxides showed some activity in a double bond shift but they were not active in the skeletal isomerization.

3.2. SUPPORTED OXIDES

It has been reported that when the γ-Al_2O_3 is partially converted to α-Al_2O_3 by heating to 1200°C for 30 min (it produces 20 m^2/g alumina), then the catalysts 1–6% WO_3/Al_2O_3 prepared by impregnation of this alumina with Na_2WO_4 and a subsequent leaching by HNO_3, show a good selectivity to isobutene [3]. The same impregnation but with γ-Al_2O_3 and also the same reduction at 400°C overnight in hydrogen flow saturated by water were applied here. However, the 5% WO_3/γ-Al_2O_3 does not show such a good selectivity to isobutene and behaves more as a hydrogenation catalyst (see table 4). Increasing the loading of WO_3 on γ-Al_2O_3 to 30% produces catalysts of a rather good selectivity to isobutene (about 20%, see table 4).

The impregnated catalysts 2–30% MoO_3/Al_2O_3 are active in the skeletal isomerization of *n*-butene, but with a rather low selectivity and with an appreciable amount of butanes. This holds also for the MoO_3 loading of 30% (table 3). Increasing of the reduction temperature to 500°C shows a positive effect, as can be seen in fig. 1.

The other impregnated catalysts as Cr_2O_3/Al_2O_3, V_2O_5/Al_2O_3 and Re_2O_7/Al_2O_3 are not active neither with the metal oxide loading as high as 30% (table 3). The "ion-exchange"-ones are slightly better (see below).

It may be noted that the oxides MoO_3 and WO_3 are also active for the skeletal isomerization when supported on silica and reduced at correct conditions, but the selectivity achieved is still lower than that with oxides supported on alumina.

The catalysts prepared as W, Mo, Cr, V and Re oxides on alumina by ion-exchange method are slightly better than the impregnated ones. The selectivities to isobutene achieved here are presented in table 4. The exchanged WO_3/Al_2O_3 containing 35% WO_3 shows the same selectivity as impregnated catalyst, in both cases about 20% isobutene (tables 3 and 4). Interestingly, this isobutene selectivity is also found to be about 20% when the catalyst is not pre-reduced at all and the carrier gas for *n*-butene is N_2 instead of H_2 (see fig. 2).

The ion-exchanged MoO_3/Al_2O_3 catalyst has the best selectivity of the various Mo catalysts producing 14% isobutene (table 4). This is higher than with the impregnated ones; it holds true at any of the different conditions of pretreatment and reaction.

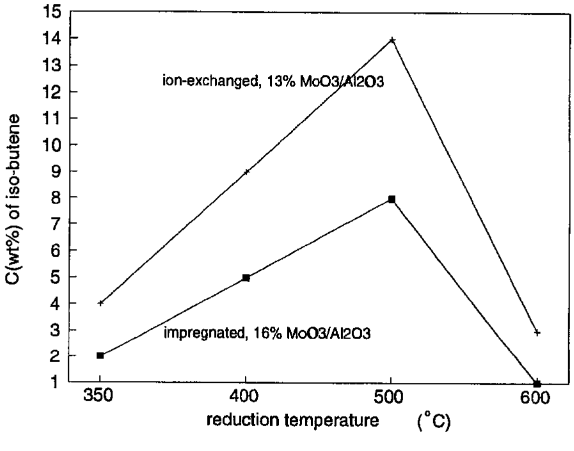

Fig. 1. Influence of the reduction temperature on the selectivity to isobutene in the *n*-butene reaction at 350°C over MoO_3/Al_2O_3 catalysts.

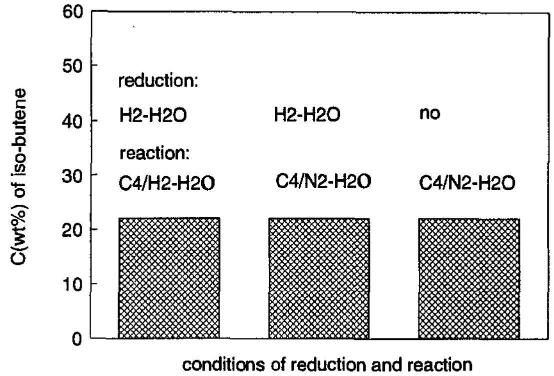

Fig. 2. Effect of reduction and reaction conditions on the selectivity to isobutene, in a reaction over the ion-exchanged WO_3/Al_2O_3 catalyst.

The best selectivity with the ion-exchanged Cr_2O_3/Al_2O_3 catalyst is 7%, achieved when the catalyst is reduced at 500°C in H_2–H_2O flow and when *n*-butene is diluted in H_2. The amount of butanes formed is very low. If *n*-butene is diluted in N_2 or H_2 saturated with water, the selectivity is lower by 50%. This most likely indicates that the reactivity of Cr_2O_3/Al_2O_3 is related to the reduced Cr species, and not to the exposed alumina support.

The ion-exchanged V_2O_5 and Re_2O_7/Al_2O_3 catalysts show a selectivity to isobutene of about 2%, what is better than the selectivity of the impregnated catalysts but it is still below the 5% obtained with pure alumina.

The results collected in table 5 concern the Mo, Ti, Zr, Nb and Ta oxides prepared from metal chlorides. First, the MoO_3/SiO_2 (prepared from chloride) containing only the grafted Mo oxide highly dispersed on silica does not show any selectivity to isobutene after having been reduced (table 5) and this is different from the MoO_3/SiO_2 catalyst containing poorly dispersed Mo oxide (table 3). Obviously, the highly dispersed Mo species could not be converted into the active phase for this skeletal isomerization, unlike the olefin metathesis reaction [6]. The Ti, Zr, Nb and Ta oxides on alumina possess some selectivities to isobutene between 6 and 24% and this is higher than the activity of the support. However, the ZrO_2/Al_2O_3 prepared from $Zr(EtO)_2$ as a Cl-free precursor has a selectivity lower than a catalyst prepared from $ZrCl_4$. Furthermore, all these catalysts made via Cl-containing precursors, lose their selectivities after having been once washed by ammonia solution. These experimental results seem to indicate that the selectivities found before washing by ammonia solution, are probably related to the chlorination of alumina by the precursor, and the oxides mentioned are actually not active in skeletal isomerization.

3.3. EFFECT OF ACETIC ACID AND ETHYLTHIOL: POISONING OF THE LEWIS SITES

As reported by us in ref. [1], molecules like CH_3COOH and $HSCH_2CH_3$ selectively and strongly poison the Lewis acid/base sites for the skeletal isomerization of the halogenated alumina. Similar experiments were also carried out on reduced MoO_3 and ion-exchanged WO_3/Al_2O_3 catalyst. The results are shown in fig. 3, indicating that the selectivity to isobutene is always strongly suppressed. This selectivity could be almost completely restored after treating catalysts poisoned by acetic acid in N_2 flow at 450°C for 30 min. However, the poisoning by $HSCH_2CH_3$ is irreversible.

3.4. CRACKING OF *n*-OCTENE

To identify the reaction pathway leading to byproducts like propene and pentenes in the *n*-butene reactions, reactions of *n*-octene were studied, too. In these experiments, 1.5% *n*-octene was diluted in the N_2 flow and its cracking reaction over γ-Al_2O_3, reduced MoO_3 and ion-exchanged WO_3/Al_2O_3 catalysts was monitored. Over the catalyst WO_3/Al_2O_3, *n*-octene is efficiently cracked down to propene, butenes and pentenes as shown in fig. 4. This could indicate that the byproducts of propene and pentenes found in *n*-butene reaction (tables 3, 4) are actually produced by a dimerization–cracking pathway. γ-Al_2O_3 is almost inactive in this reaction at 350°C since at this temperature only less than 2% of *n*-octene is cracked and the uncracked octenes are different isomers of octene. This correlates with the low amount of byproducts in *n*-butene reaction (table 2). However, the reduced MoO_3 does not produce much of byproducts in the *n*-butene reaction (table 2) but it is also able to crack *n*-octene in the presence of H_2 (see fig. 5) like WO_3/Al_2O_3 does.

4. Discussion

4.1. ACTIVITY PATTERN

To identify elements with an appreciable activity and the desired selectivity for the skeletal isomerization of *n*-butene, a search along the periods of the periodic

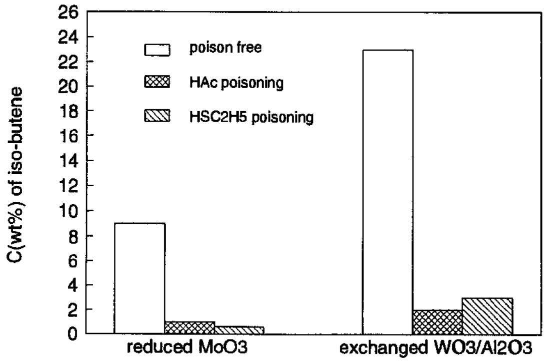

Fig. 3. Effect of poisoning the catalysts by HSC_2H_5 and CH_3COOH, on the selectivity to isobutene.

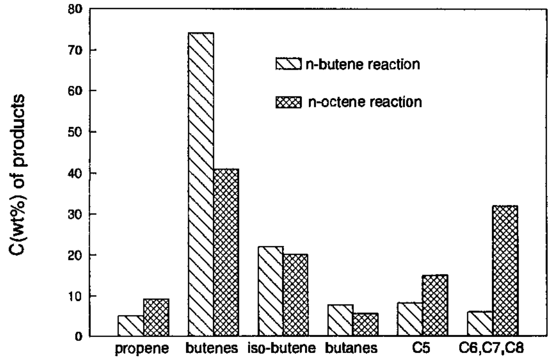

Fig. 4. Distribution of products in the reactions of *n*-butene and *n*-octene over WO_3/Al_2O_3 catalyst at 1 h on stream.

system has been performed. It is now known that the group VIA (Cr, Mo and W) oxides and the Al oxide are potentially active catalysts. In addition, activations like that by halogenation, or by sulfuric or phosphoric acids, can also produce active catalysts [7,8]. The chlorinated or brominated alumina has the highest selectivity to isobutene at the low temperature of 350°C [1].

4.2. MECHANISM OF SKELETAL ISOMERIZATION

Suggestions in the literature with regard to the mechanism, can be categorized into two main groups: (i) the monomolecular type mechanisms, (ii) a bimolecular mechanism. When (ii) operates, olefin dimerizes first, isomerizes thereafter and is cracked down back to C_4-fragments, with an unavoidable formation of byproducts. Among the byproducts, propene and pentenes should be the most abundant ones. The group of monomolecular mechanisms can be subdivided into the following subgroups:

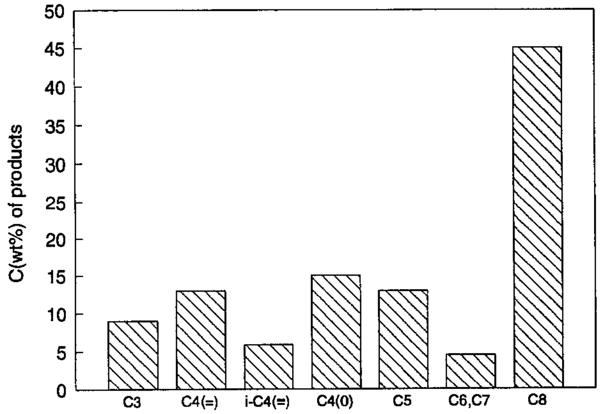

Fig. 5. Distribution of products over unsupported and reduced MoO_3 in *n*-octene reaction at 350°C.

(1) An olefin is converted into an *allyl-like species*, which is then the key intermediate of isomerization. Occupation by electrons of the orbitals of the allyl-like species is not evident, but the results gathered up to now are compatible with the formation of allyl anions, as intermediates [1].

(2) An olefin forms a substituted cyclobutallo-metal ion species, which in its turn can be split into *carbene* and *π-complexed olefinic fragments*. This splitting is reversible, the original molecule can be reconstituted, or, when the π-complexed olefinic fragment has been – in the mean time – displaced by olefinic reactant, a C_{n+1} olefin desorbs. This is the generally accepted mechanism of olefin metathesis (see ref. [9] for a review). If one assumes that carbene species can be also added to the internal and not only to the terminal position on the olefinic fragment, isomerized products should be formed by this mechanism. This mechanism would be compatible with the results and ideas presented by Weeks and Bolton [10].

(3) With the two above mentioned mechanisms, the organic molecule is being held on the cation of the catalyst. However, it is also possible that the interaction of an olefin with the surface starts by the formation of an *alkoxy species*, which is by the subsequent steps converted into allyl-like species or which itself isomerizes directly [11].

(4) A *classic acidic ionic mechanism* [7].

There are pro's and contra's for each of the mechanisms suggested. The weakest is the support for the last mechanism (4). With a C_4-olefin, this mechanism implies formation of a primary ion and that is not a very likely step. From the presented list of mechanisms, the mechanism (3) can be considered as an alternative for the primary carbenium mechanism and would imply a formation of some kind of cyclopropane-like rings. This is certainly a possibility (see fig. 6) and the main disadvantage of this mechanism is the lack of an independent evidence for the speculative conversion of the alkoxy species. Further, one would expect a higher extent of hydrogenation when the reaction is performed in hydrogen flow, than found experimentally with most of the catalysts.

The carbene (metathesis-like) mechanism seems to be a rather attractive possibility of explanation for the appreciable activity of the suitably activated Mo- and W-oxides. On the other hand, the virtual lack of activity of Re-oxide should be then explained by saying that a proper way of activation has not been found yet, since Re-oxide activated by certain hydrocarbons is a good catalyst of metathesis.

Having in mind the literature on Al_2O_3, one would not immediately suggest a metathesis-like mechanism for this oxide. However, the results obtained in ref. [10] have lead the authors to suggest a transfer of C_1-units amongst the adsorbed molecules as a part of a more complicated general mechanism operating on acidic catalysts. An allyl-like species can – in principle – induce such mechanism, too. When inspecting closely the various product distributions shown in tables 2–4 we are inclined to admit, that the so-called bimolecular mechanism contributes something to the overall mechanism (see the C_3 and C_5 formation). However, it is most likely not the main mechanism.

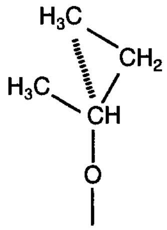

Fig. 6. A proposed formation of a cyclopropane-like ring from alkoxy species. Dotted line indicates the bond formation in subsequent steps, which involve also an intramolecular hydrogen atom migration.

Obviously, the data gathered in this and the previous paper [1] do not allow to decide definitively in favour of one or another mechanism. It is the hope that further accumulation of experimental data will allow to do so in the future.

4.3. ACTIVE SITES

Identification of the active sites is closely related to the establishing of the mechanism. Since not much of definitive conclusions exist on the latter question one cannot expect too much with regard to the identity of the active sites. Nevertheless, some information on this subject can be already extracted from the results in this and the earlier paper [1].

Without doubt, a certain electronic structure of the cation of an oxide is required. First, only a limited number of oxides are active, at all. For example, Al_2O_3 can be more easily activated for the title reaction than – for example – the rare earth sesquioxides, in spite of a certain similarity between these oxides. Another preliminary conclusion which can be drawn at the moment is that a certain heat – and hydrogen – treatment is beneficial for the activity in the skeletal isomerization. The most likely effect of such treatment is a removal of some OH groups and oxy-anions and a creation of a defective structure of the oxide in question. This is in particular demonstrated by a comparison of results concerning three types of Mo- and W-oxide catalysts; the activity can be most easily induced in Al_2O_3-supported catalysts while the unsupported catalysts represent the other extreme. The defects can be suspected to stimulate any of the monomolecular mechanisms presented under (1) to (3) in the above list, but it is not possible to go any further beyond these conclusions.

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