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Selective isomerisation of *n*-butene by crystalline aluminophosphates

L.H. Gielgens, I.H.E. Veenstra, V. Ponec [1]

Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502,
2300 RA Leiden, The Netherlands

M.J. Haanepen and J.H.C. van Hooff

Schuit Institute of Catalysis, Eindhoven University of Technology, PO Box 513,
5600 MB Eindhoven, The Netherlands

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The results presented in this paper demonstrate that Me-$AlPO_4$-11's are active, selective and stable catalysts for the selective isomerisation of *n*-butene to isobutene. A suggestion is given for an active site. The results support a monomolecular reaction mechanism. Absorption experiments of *n*-butene on Me-$AlPO_4$-11 and Me-$AlPO_4$-5 are presented, indicating that under the reaction conditions butene polymerisation occurs on Me-$AlPO_4$-5 leading to a rapid deactivation.

Keywords: isobutene; skeletal isomerisation; aluminophosphates; Me-$AlPO_4$-11

1. Introduction

Under the increasing pressure of society and its legislature, liquid fuels have to be newly formulated. No lead compounds may be added and the content of aromatics is limited, therefore the high octane number had to be achieved by other compounds. Complete combustion (suppression of CO-emission) of the fuel has to be promoted by oxygen-containing additives. An ideal additive seems to be methyl tertiary-butyl ether (MTBE) which meets all the requirements simultaneously. Consequently, there is a high demand for this compound which is easily produced from isobutene. In its turn, isobutene would be most conveniently produced by skeletal isomerisation of *n*-butene.

Skeletal isomerisation of *n*-butene is, indeed, possible [1–5] and a carbenium ion mechanism is usually postulated to operate [1–4]. Since the C_4-hydrocarbons can isomerise only by formation of a primary carbenium ion, a step which is consid-

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[1] To whom correspondence should be addressed.

ered as very difficult or even impossible [6,7], it has been suggested that the mechanism is actually "bi-molecular": butene forms a secondary carbenium ion which induces dimerisation to octenes, which thereafter isomerise freely and are subsequently cracked to $C_4^=$, without formation of the primary carbenium ion [8–10].

Cheng et al. [11,12] studied the skeletal isomerisation on series of oxides (supported and unsupported ones) and on halogenated alumina's. They conclude that the bimolecular mechanism is in principle possible but it leads to undesired side reactions (C_3 and C_5) products while a more selective monomolecular mechanism clearly prevails with most of the catalysts studied. This casts serious doubts on the operation of the carbenium ion mechanism and the identity of the active sites is now an open question.

Recently, metal-substituted crystalline aluminophosphates have been studied and the character of the potentially-active sites has been established [13–18]. This knowledge can be used to advantage in the discussion of the mechanism of skeletal isomerisation on these zeolites.

2. Experimental

The Me-$AlPO_4$-5 and Me-$AlPO_4$-11 molecular sieves (Me loading ≈ 1 wt%) used in this study have been prepared hydrothermally in a static teflon lined autoclave at 190°C following instruction given in the literature [16,19]. Pseudoboehmite (Condea), the appropriate metal salt, phosphoric acid (85%) and the organic template (triethylamine for $AlPO_4$-5, diisopropylamine for $AlPO_4$-11) have been added successively under high shear mixing. X-ray diffraction measurements showed all samples to be highly crystalline and pure.

Catalytic measurements have been performed in a continuous flow, fixed bed reactor at a total pressure of 1 bar. Conditions of a standard test are: 500 mg catalysts, $T = 400°C$, total flow = 20 ml/min, 1-butene pressure 0.1 bar, nitrogen used as diluting inert gas. Dimerisation experiments were performed at 80°C, with a pure 1-butene or isobutene feed (flow: 20 ml/min).

Analysis has been done by gas chromatography. Catalytic behaviour of the catalysts used was evaluated in a simple way on basis of the FID signal intensities (I). The selectivity to isobutene is defined as

$$S_{\text{iso}}\ (\text{wt\%}) = 100 \times \left(I^{\text{isobutene}} \Big/ \sum I^{\text{products}}\right), \qquad (1)$$

where "products" indicates that only products of the 1-butene reaction are considered. Since the FID signal intensity is proportional to the number of carbon atoms, we can speak essentially of wt%. Conversion is defined as

$$\alpha\ (\%) = 100 \times \left[I^{\text{1-butene}} \Big/ \left(I^{\text{1-butene}} + \sum I^{\text{products}}\right)\right], \qquad (2)$$

where $I^{\text{1-butene}}$ stands for 1-butene signal. The product $\alpha S/100$ is called yield.

Absorption of 2-butene on Me-$AlPO_4$- was studied using a Cahn 2000 Electro-

Table 1
Yields (wt%) at 400°C in a standard test after 16 h on-stream of the (Me-)$AlPO_4$-11 catalysts

Products	$AlPO_4$-11	Mn-$AlPO_4$-11	Co-$AlPO_4$-11	Mg-$AlPO_4$-11
C_1, C_2	<1	<1	<1	<1
C_3	<1	3	6	7
butane	<1	<1	<1	<1
n-butene	88	54	46	47
isobutene	6	42	41	41
C_{5+}	<1	<1	3	3

balans. About 25 mg of sample was dried in a helium flow at 350°C. After cooling to room temperature the start weight G_{start} (mg) was determined. Subsequently, the sample was heated to the desired reaction temperature and 2-butene, diluted in helium (total He-flow: 135 ml/min; 2-butene flow: 18 ml/min) was contacted with the sample for 1 h. Afterwards the sample was cooled to room temperature to determine the final weight of the sample (G_{end} (mg)). Finally all weakly bound products were removed by heating the sample at 350°C in helium for 30 min. After cooling of the sample to room temperature the pore volume of the sample was determined by absorption of *n*-butane (V_{end}). The pore volume of a fresh sample (V_{start}) was determined in a separate experiment.

3. Results

The selectivities to isobutene of pure $AlPO_4$-11 and $AlPO_4$-5 were very low. Both catalysts showed almost only linear isomerisation activity. The metal-substituted crystalline aluminophosphates derived from $AlPO_4$-11 appeared to be very

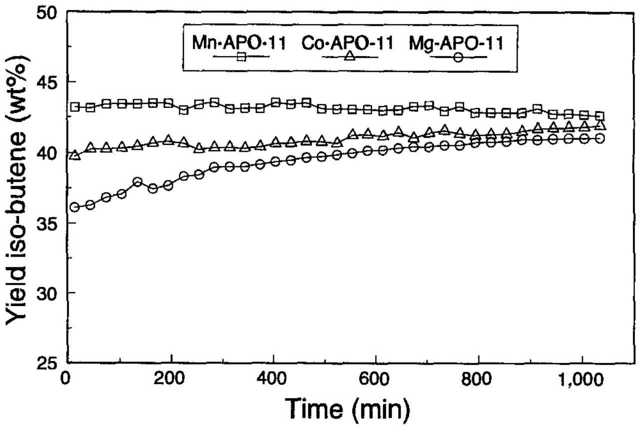


Fig. 1. Isobutene yield (wt%) versus time-on-stream at 400°C of the different metal-substituted Me-$AlPO_4$-11 catalysts.

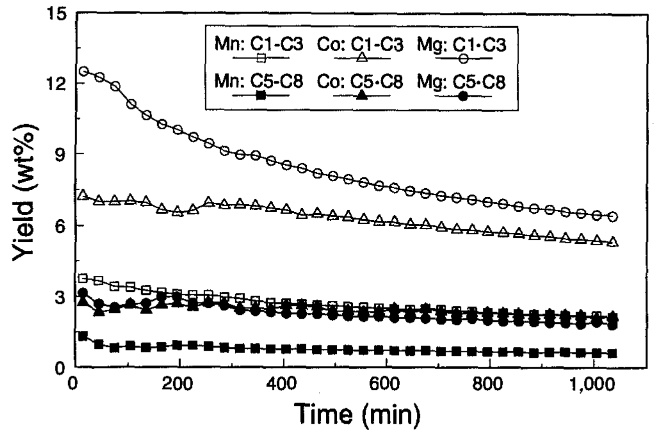


Fig. 2. Byproduct production (wt%) versus time-on-stream at 400°C of the different metal substituted Me-AlPO$_4$-11 catalysts.

active, selective and stable catalysts for the skeletal isomerization of *n*-butene at 400°C (see table 1 and figs. 1 and 2). In contrast, metal-substituted catalysts derived from AlPO$_4$-5 appeared to be substantially less active in skeletal isomerisation. Similar to the pure AlPO$_4$-'s, selectivities to isobutene of less than 5% were found.

It has to be noticed that the Me-AlPO$_4$-11 catalysts showed their high stability only when they were tested at 400°C, at 250°C deactivation occurred (fig. 3). This type of temperature dependent deactivation is most likely due to the occurrence of oligomerisation at low temperatures. As the test at 80°C revealed, dimerisation is indeed occurring with the catalysts studied. The extent of dimerisation can be seen in table 2.

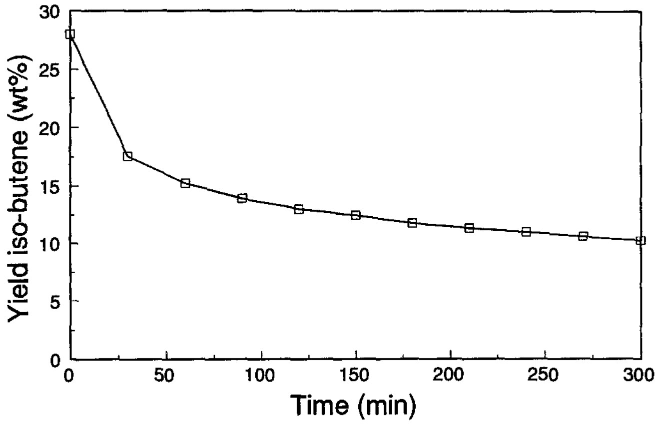


Fig. 3. Isobutene yield (wt%) versus time-on-stream at 250°C of the catalyst Co-AlPO$_4$-11.

Table 2
Conversion of 1-butene and isobutene (%) over Me-AlPO$_4$-11 catalysts at 80°C (feed: 100% olefin). The product distribution of di- and oligomerisation (in % of carbon appearing in di- and oligomers) contains a broad range of indicated hydrocarbons

	Mn-AlPO$_4$-11	Co-AlPO$_4$-11	Mg-AlPO$_4$-11
feed 1-butene			
conversion (%)	70	60	50
C_6/C_7 products (wt%)	21	24	33
C_8 products (wt%)	31	25	18
feed isobutene			
conversion (%)	30	70	30
C_6/C_7 products (wt%)	18	29	19
$\geqslant C_8$ products (wt%)	12	42	4

It is important to add that this di/oligomerisation is (i) not selective to a (few) specific C_8-product(s), but instead a broad range of hydrocarbons are formed and (ii) dimerisation of the more bulky isobutene is with Mn and Mg-AlPO$_4$-'s more difficult than dimerisation of 1-butene.

Absorption experiments using 2-butene also showed a remarkable difference between Me-AlPO$_4$-5 and Me-AlPO$_4$-11, as shown in table 3. The pore volume of Me-AlPO$_4$-11 was almost unchanged after the standard experiment at 400°C, while the pores of Me-AlPO$_4$-5 are blocked irreversibly. The absorption behaviour depends strongly on the temperature. With decreasing the temperature the extent of absorption increases. At 25°C the pores are almost completely filled with butenes and products formed at that temperature. However, most of these products desorb at 350°C in helium flow in the case of Me-AlPO$_4$-11.

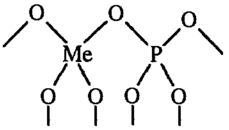
Table 3
Absorption behaviour of *n*-butene on Me-AlPO$_4$-11 and Me-AlPO$_4$-5

Sample	T_{reaction} (°C)	G_{start} (mg)	G_{end} (mg)	Δ[a] (mg)	V_{start} (ml/g)	V_{end} (ml/g)
Co-AlPO$_4$-5	80	23.92	24.46	0.54	0.106	0.080
Co-AlPO$_4$-5	250	23.32	23.56	0.24	0.106	0.065
Co-AlPO$_4$-5	400	21.54	22.30	0.76	0.106	0.0
Mn-AlPO$_4$-5	400	26.63	27.86	1.23	0.091	0.0
Mn-AlPO$_4$-11	25	22.04	22.94	0.90	0.060	0.053
Mn-AlPO$_4$-11	80	24.62	25.10	0.48	0.060	0.058
Mn-AlPO$_4$-11	250	26.34	26.52	0.18	0.060	0.044
Mn-AlPO$_4$-11	400	25.26	25.28	0.02	0.060	0.053
Co-AlPO$_4$-11	400	22.51	22.60	0.09	0.043	0.025
Mg-AlPO$_4$-11	400	21.66	21.69	0.03	0.048	0.039

[a] $\Delta = G_{\text{end}} - G_{\text{start}}$.

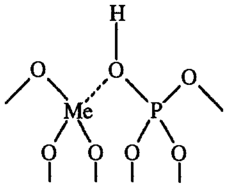
4. Discussion

Unsubstituted aluminophosphates have a very low selectivity to isobutene. After metal substitution (Mn, Co or Mg) a sharp increase in isobutene production is observed with $AlPO_4$-11's. This means that the active sites are generated by metal substitution into $AlPO_4$-11. Previous work done in the characterisation of the metal-substituted crystalline aluminophosphates [13–18] enables a start of the discussion on the nature of these active sites and on the mechanism of the skeletal isomerisation. With the aluminophosphates studied, the incorporation of tri-, bivalent metal ions can lead to the following (schematically shown) structures. Structure I is formed with metal ions in oxidation state 3 (e.g. Mn^{3+} and CO^{3+}), while structure II is formed with the bivalent ions (e.g. Mn^{2+}, Co^{2+} and Mg^{2+}).



Me= 3+

Structure I



Me= 2+

Structure II

It has been reported [16] that Me^{3+}-$AlPO_4$-'s are very easily reduced by organic molecules like C_2H_4 or CH_3OH and it can be expected that the same holds for butenes. On the other hand, reduction of Me^{3+} by H_2 or CO is more difficult. Reduction by hydrocarbons is so easy that it occurs at room temperature and therefore we can ignore the possible existence of structure I under reaction conditions. Moreover, the similarity between Mn, Co and Mg-$AlPO_4$-11's, from which the Mg-cation in Mg-$AlPO_4$-11 exists only in oxidation state 2, makes structure II most likely to exist under reaction conditions.

Structure II, consisting of isolated P-OH group together with the adjacent divalent metal ion as Lewis site, should be considered as the potential active site. The substituted Me^{2+} cation is at first glance a good candidate but the fact that so much different cations as Mg^{2+} on one side and Mn^{2+}, Co^{2+} on the other side show very similar properties seems to be an argument against this possibility. It is more likely the modification of the zeolite caused by metal substitution (e.g. formation of the P-OH groups) rather than the cation itself should be related to the activity of the substituted $AlPO_4$-'s. The *combination* of a Lewis site next to the P-OH group could of course also be *the* active site. The outer surface of $AlPO_4$-11 consists of P-OH and Al-OH. The presence of these P-OH or Al-OH alone is not enough to induce high selectivity. In either way, we consider the presence of the P-OH group as absolutely necessary.

It is known that C_2D_4 dimerises on Co-$AlPO_4$-'s, but it does not exchange its deuterium with the OH-groups of the catalysts [16]. When a catalyst shows a strong

Brønsted acidity, the H–D exchange with deuterated ethene occurs freely upon dimerisation, what can be considered as an indication that the dimerisation is induced by carbenium-ion formation. The dimerisation by Me-$AlPO_4$-'s thus most likely occurs by an appropriate radical mechanism or between π-complexed olefins. Oligomerisation through π-complexed intermediates or adsorbed radicals formation (if these can exist) is most likely related to the different cations in the catalyst. There is indeed a significant difference in dimerisation activity between the various Me-$AlPO_4$-11 samples. Oligomers, when formed, block the skeletal isomerisation, what we derive from the comparison of fig. 3 and table 3, so that the active site for oligomerisation or polymerisation, the cation, is probably located near the site active in skeletal isomerisation, or it is perhaps even the same site. This supports the idea that the P-OH group possibly next to the Lewis site, or the combination of both sites, is the active site for butene isomerisation.

The presented results stimulate us to speculate about the isomerisation mechanism on Me-$AlPO_4$-11. Dimerisation of 1-butene over Me-$AlPO_4$-11's is possible, but it is a very unselective pathway. As a consequence the dimerisation–cracking mechanism would always result in a high byproduct level, what is not found experimentally. Furthermore, a relatively small fraction of isobutene dimerises, which indicates that formation of branched C_8 molecules in the Me-$AlPO_4$-11 pores is difficult. These results suggest that the isomerisation mechanism is not bimolecular (e.g. a dimerisation–cracking mechanism) but monomolecular.

It is known [20] that the phosphor–alkoxy band is formed very easily, so that an alkoxy-like intermediate is possible. However, there is also an alternative mechanism possible: *n*-butene is converted into an allyl-intermediate which could be another potential intermediate [11] of skeletal isomerisation, in particular in its anionic form [21]. Both just mentioned mechanisms can in principle also operate on WO_{3-x} catalysts [5,22] and on halogenated aluminas [12].

A small detail of the observation made with Mg-$AlPO_4$-11 deserves attention. With increasing time-on-stream a slight increase in isobutene selectivity is observed, and in parallel we see a decrease in C_3/C_5 byproduct formation (figs. 1 and 2). Probably, sites responsible for the bimolecular mechanism, e.g. strong Brønsted acid sites, deactivate on-stream. The more selective monomolecular mechanism becomes (even) more important, and consequently less byproducts are formed [11,12]. With supported tungsten oxide catalysts, a simultaneous decrease of isobutene and C_3/C_5 hydrocarbon formation has been seen [22]. In this case, byproducts are probably formed after secondary dimerisation and subsequent cracking of isobutene. Due to pore size restrictions, dimerisation of isobutene is more difficult in crystallinic aluminophosphates compared to supported tungsten oxide catalysts.

The difference in activity and selectivity in *n*-butene isomerisation between Me-$AlPO_4$-11's and Me-$AlPO_4$-5's is surprising and is not well understood yet. Especially, because structure II, and so the potential active site, is identical for both systems. It has been argued that the differences in pore size between $AlPO_4$-5 and

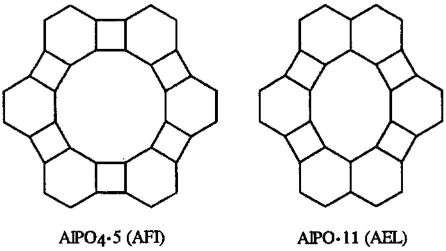


Fig. 4. Pore structures of $AlPO_4$-5 (left) and $AlPO_4$-11 (right). The pore size of $AlPO_4$-5 is about 7.3 × 7.3 Å, the pores of $AlPO_4$-11 are 6.3 × 3.9 Å.

$AlPO_4$-11 ($AlPO_4$-5's have larger pores, compared to $AlPO_4$-11's) explain the observed discrepancy (fig. 4) [23]. Indeed, as demonstrated in table 3 the large pores of Me-$AlPO_4$-5 are irreversibly filled after 1-butene admittance at 400°C, while the smaller pores of Me-$AlPO_4$-11 remain always accessible. After a short time on-stream *n*-butene cannot reach the potential active site in Me-$AlPO_4$-5, and consequently no isobutene is formed.

5. Conclusions

(i) It is found that crystalline Me-$AlPO_4$-11's are active, selective and stable catalysts for skeletal isomerisation of *n*-butene.

(ii) The related Me-$AlPO_4$-5's are not good catalysts for the skeletal isomerisation, because the "large" pores are blocked irreversibly with *n*-butene reaction products.

(iii) It is argued that the results of this paper strongly indicate that the active site is a weakly acidic OH-group, possibly in the neighbourhood of or in combination with a Lewis acid site.

(iv) There are strong indications that the mechanism is "monomolecular".

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