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Fluorinated metal oxide-assisted oligomerization of olefins

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Fluorinated alumina is an efficient catalyst for hex-1-ene, cyclohexene and isobutene oligomerization, whereas fluorinated titania and zirconia are inactive.

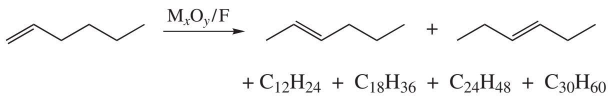
Solid superacids represent a unique class of materials which exhibit an acid strength higher than that of 100% sulfuric acid ($H_0 = -11.93$).[1,2] Higly acidic sulfated metal oxides find use as solid superacids because of ease of their preparation. The main drawback of sulfated oxides is a fast Me–O–S bonds hydrolysis, so their catalytic activity can vary considerably. Fluorination instead of sulfation was suggested as an alternative for the modification of acidity and, subsequently, activity and stability of solid superacids.[3,4]

Fluorinated acid catalysts can be conventionally divided into two groups: (i) fluorinated oxides;[3,5–7] and (ii) pure fluorides, AlF_3 being the most investigated among them.[8–11] We could not find any data concerning the Hammet acidity determination of fluorinated catalysts.

We decided to investigate fluorine-modified oxides in the reaction with selected olefins with the aim to find novel catalysts for oligomerization of lower olefins to liquid materials, *e.g.*, ethene → butenes → hexenes + octenes.[†]

Hex-1-ene was chosen as a model long-chain terminal olefin (Scheme 1, Table 1).

As can be seen, all fluorinated Al_2O_3 samples have a relatively high catalytic activity which practically does not depend on starting NH_4F solution concentration. The lowest content of C_6 olefins was observed for entry 7. This means that raising the temperature causes further transformation of hexenes into higher oligomers (entries 5–7). Surprisingly, fluorinated Al_2O_3 appeared to be the only active catalyst, whereas fluorinated ZrO_2 and TiO_2 were not catalytically active even at 60 °C. The result is rather unusual because the corresponding sulfated oxides have approximately the same or even higher acid strength than sulfated alumina.[13]



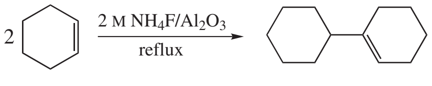
Scheme 1

Table 1 Hex-1-ene and cyclohexene oligomerization.

Entry	Catalyst	t/h	T/°C	Conversion (%)	C_6–C_{30} selectivity (%)				
					C_6	C_{12}	C_{18}	C_{24}	C_{30}
1	Al_2O_3	24	25^a–60	0					
2	0.5 M NH_4F/Al_2O_3	2	25^a	52					
3		24	25^a	100	35	27	27	9	2
4		2	25^a	64	—[b]	—[b]	—[b]	—[b]	—[b]
5	2 M NH_4F/Al_2O_3	24	25^a	88	34	24	29	9	4
6		1	40	100	26	26	36	10	2
7		1	60	100	2	32	46	14	6
8	5 M NH_4F/Al_2O_3	2	25^a	32	—[b]	—[b]	—[b]	—[b]	—[b]
9		24	25^a	100	37	25	26	8	4
10[c]	2 M NH_4F/Al_2O_3	6	83			29^d			
11	2 M NH_4F/TiO_2	1–24	25–60	0					
12	2 M NH_4F/ZrO_2	1–24	25–60	0					

[a] Room temperature. [b] Chromatographic analysis of products was not performed. [c] Cyclohexene as a substrate. [d] 1-Cyclohexylcyclohexene yield.

A catalytic activity of fluorinated Al_2O_3 was also tested on internal C=C bond-containing cyclic olefin, namely cyclohexene (Scheme 2). We have found that fluorinated Al_2O_3 afforded cyclohexene dimer in 29% yield (Table 1, entry 10).



Scheme 2

Isobutene oligomerization process may be of industrial interest because resulting isoolefins can be hydrogenated to isooctane and analogues (Scheme 3). Earlier isobutene oligomerization on a solid superacid TiO_2/SO_4 was performed under pressure.[14] We have oligomerized isobutene in a flow reactor under normal pressure at 150 °C using 2 M NH_4F/Al_2O_3 as a catalyst. The

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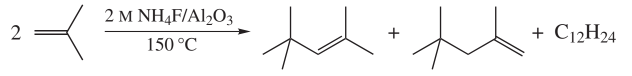
[†] Al_2O_3 was purchased from Engelhard (E-800). ZrO_2 and TiO_2 were prepared by standard procedures.[12] Oxide (4 g) and 100 ml of 0.5, 2 or 5 M aqueous solution of NH_4F were stirred in a teflon flask for 1 h at room temperature, filtered off and dried at 100 °C. A catalyst sample (1 g) was pre-conditioned in air at 600 °C for 2 h and then cooled in a dry atmosphere. A catalyst and 0.1 mol of an olefin were placed into a water-jacketed glass flask and kept at constant temperature under vigorous stirring. Samples of a reaction mixture were periodically taken for ^1H NMR and GC-MS analysis.

Surface acidity (H_0) was estimated by a Hammett-indicator method in SO_2Cl_2 using *m*-nitrotoluene ($H_0 = -11.99$), *p*-nitrochlorobenzene ($H_0 = -12.7$), and 2,4-dinitrotoluene ($H_0 = -13.75$) as indicators.[2]



Scheme 3

conversion was 87% in 4 h, 90% of the products were $C_8 + C_{12}$ fraction.

X-ray diffraction studies showed that initial alumina had cubic structure (PDF #10-425) (Figure 1).[‡] Upon washing in diluted NH_4F solutions (0.5 M and 2 M) and subsequent thermal treatment, the crystalline structure of powders did not change. Treatment with 5 M NH_4F solution followed by calcination at 600 °C resulted in a partial formation of anhydrous aluminium fluoride. Thus, the sample obtained from concentrated solution of NH_4F is biphasic. Particle size of aluminium fluoride estimated using Scherrer equation was about 20 nm.

According to EDX data, fluorine to aluminium molar ratio at the surface of the fluorinated alumina catalysts increased from 1:4 to 2:1 with the increase in NH_4F concentration. These data are in a good agreement with the tendency revealed by XRD study. Fluorine to titanium molar ratio at the surface of the fluorinated titania catalyst was 1:8, fluorine to zirconium molar ratio at the surface of the fluorinated zirconia catalyst was 1:7, revealing that fluorination of alumina surface proceeds much more effectively compared to zirconia and titania.

The Hammet acidity function H_0 is used as a measure of acid strength in nonaqueous solvents. Values less than H_0 for 100% H_2SO_4 (–11.93) are considered superacidic.[1] The determination of the Hammet acidity function H_0 revealed that the acidity of NH_4F/Al_2O_3 samples reached the value of *ca.* –13.75; it means that fluorinated Al_2O_3 can be considered as a solid superacid.[1] Fluorinated TiO_2 (H_0 is *ca.* –12.7) and ZrO_2 (H_0 is *ca.* –11.99) appeared to be substantially weaker acids than fluorinated alumina.

The surface area and H_0 values of catalysts samples are presented in Table 2.

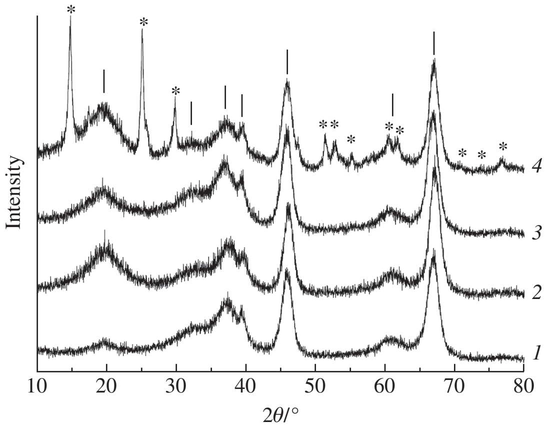


Figure 1 X-ray diffraction data for samples of fluorinated alumina: (*1*) initial alumina powder, (*2*)–(*4*) alumina powder after washing with 0.5, 2.0 and 5.0 M NH_4F solution, respectively, followed by thermal treatment at 600 °C. Asterisks point diffraction peaks of AlF_3 (PDF #43-435), dashes – Al_2O_3 (PDF #10-425).

Table 2 The surface area and H_0 values of catalysts samples.

Catalyst	H_0	Surface area/ $m^2 g^{-1}$ (±15%)
Al_2O_3	—[a]	150
0.5 M NH_4F/Al_2O_3	~ –13.75	145
2 M NH_4F/Al_2O_3	$-13.75 < H_0 < -12.7$	180
5 M NH_4F/Al_2O_3	> –12.7	120
TiO_2	—[a]	15
2 M NH_4F/TiO_2	~ –12.7	20
ZrO_2	—[a]	30
2 M NH_4F/ZrO_2	~ –11.99	20

[a] Not determined.

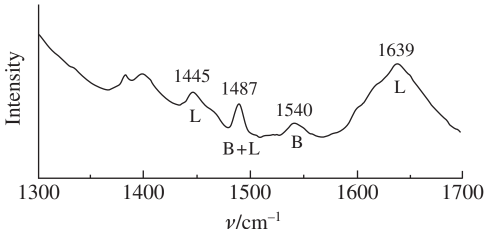
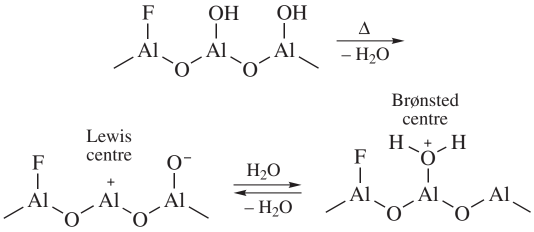


Figure 2 IR spectroscopy data of pyridine adsorbed on a surface of the 2 M NH_4F/Al_2O_3 catalyst.

To determine the types of acidic centres of the 2 M NH_4F/Al_2O_3 catalyst, we used IR spectroscopy data of pyridine adsorbed on a surface (Figure 2).[§] The IR spectra of fluorinated alumina samples contained bands which are characteristic of pyridinium ions adsorbed on both Lewis (L) and Brønsted (B) acid centres (cm^{-1}): 1445 (L), 1490 (B + L), 1540 (B), 1639 (L).[15] We suppose that Lewis and Brønsted acid sites are formed according to a mechanism offered for sulfated oxides[2] (Scheme 4).



Scheme 4

The IR spectra of fluorinated titania and zirconia did not show adsorbed pyridinium ions at all. This may be due to a very low concentration of surface acidic centres.

A catalytic activity of fluorinated oxides is a function of their acidity. Fluorinated alumina has a higher acid centres concentration in comparison with those for fluorinated titania and zirconia, and alumina centres are more acidic. We suppose that at least two factors determine the absence of catalytic activity of fluorinated titania and zirconia: (i) a low F : Ti/Zr ratio due to a thermohydrolytic cleavage of Ti–F or Zr–F bonds during their calcination at high temperature and (ii) significantly lower specific surface area which cannot provide enough accessibility of substrate to acidic centres.

In conclusion, soaking of alumina in aqueous NH_4F solution with subsequent calcination can be used as a simple and effective route to produce superacidic fluorinated alumina which appeared to be an effective acid catalyst for olefin oligomerization.

[‡] Powder X-Ray diffraction (XRD) analysis was carried out on a Rigaku D/Max 2500 diffractometer with a rotating copper anode (CuKα irradiation, $5° \leqslant 2\theta \leqslant 80°$, 0.02° step). Diffraction maxima were indexed using the PDF-2 database. Energy dispersive X-Ray analysis (EDX) was performed using a field emission scanning electron microscope Carl Zeiss NVision 40 equipped with Oxford Instruments X-MAX analyzer operating at 20 kV accelerating voltage.

[§] IR spectroscopy was performed on a Spectrum One (Perkin Elmer, USA) spectrometer in a 4000–350 cm^{-1} region (KBr pellets, 0.25–0.5% mass sample content). Samples for IR analysis were prepared as follows. A catalyst sample (~0.04 g) was calcined in a dry air flow in a tube reactor at 600 °C. After that the temperature was decreased to 150 °C, a bubbler with 1 ml of pyridine was embedded into the air line and a resulting gas-pyridine mixture was passed over the catalyst sample until all pyridine was evaporated.

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