ISSN 0020-1685, Inorganic Materials, 2014, Vol. 50, No. 5, pp. 479–481. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © L.L. Yurkova, S.A. Lermontov, A.N. Malkova, A.E. Baranchikov, V.K. Ivanov, 2014, published in Neorganicheskie Materialy, 2014, Vol. 50, No. 5, pp. 518–521.

1-Hexene Oligomerization by Fluorinated Tin Dioxide

L. L. Yurkova[a], **S. A. Lermontov**[a], **A. N. Malkova**[a], **A. E. Baranchikov**[b], **and V. K. Ivanov**[b, c]

[a] *Institute of Physiologically Active Compounds, Russian Academy of Sciences,*
Severnyi proezd 1, Chernogolovka, Noginsk district, Moscow region, 142432 Russia
[b] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,*
Leninskii pr. 31, Moscow, 119991 Russia
[c] *Moscow State University, Moscow, 119899 Russia*
e-mail: lermontov52@yandex.ru

Received November 12, 2013

Abstract—Fluorinated tin dioxide has been shown to exhibit catalytic activity for 1-hexene oligomerization. The physicochemical and functional properties of nanocrystalline fluorinated SnO_2 have been studied.

DOI: 10.1134/S0020168514050215

INTRODUCTION

The use of liquid mineral acids as industrial catalysts inevitable [1, 2] leads to the generation of a large amount of waste. Moreover, such acids are highly corrosive and toxic. For this reason, there is currently great practical interest in the development of new heterogeneous catalysts free of these drawbacks and possessing high activity. Possible candidates include sulfated metal oxides, which possess highly acidic properties [3–5] due to the strong electron acceptor effect of the SO_4^{2-} group. At the same time, M–O–S bonds readily hydrolyze, which makes such catalysts sensitive to the presence of moisture in the reaction mixture.

In this context, fluorinated oxide catalysts appear sufficiently attractive because they are less susceptible to hydrolysis and because the electron acceptor properties of the fluoride ion are at least comparable to those of the sulfate ion.

The activity of fluorinated acid catalysts has been studied to date for a rather limited range of reactions. In particular, a number of practically important processers, such as dealkylation of aromatic compounds and alkane isomerization, remain unexplored. Alkene oligomerization, a promising process for the preparation of liquid fuel from lower hydrocarbons, has only been carried out on fluorinated alumina [6].

The objectives of this work were to prepare nanocrystalline fluorinated tin dioxide, investigate its physicochemical properties, and assess its catalytic activity for 1-hexene oligomerization. Fluorinated tin dioxide was chosen as the subject of this study because its sulfated analog (SnO_2/SO_4) exhibited very high acidity (exceeding that of sulfated alumina) and catalytic activity for isobutene, 1-hexene, and cyclohexene oligomerization [3]. Note that fluorinated tin dioxide films feature high electrical conductivity and are used in photoelectrochemical solar power converters [7].

EXPERIMENTAL

The phase composition of the solid samples was determined by X-ray diffraction on a Rigaku D/MAX 2500 diffractometer (CuK_α radiation, 2θ scan rate of 2°/min). The crystallite size of the tin dioxide samples was determined using the Scherrer formula, with instrumental broadening taken into account.

Specific surface areas (S) were determined by low-temperature nitrogen adsorption measurements with an ATX-06 analyzer (KATAKON, Russia). Prior to measurements, the samples were outgassed at 200°C in flowing dry helium for 30 min. The specific surface of the powders was evaluated using Brunauer–Emmett–Teller (BET) analysis (six points).

^1H NMR spectra in $CDCl_3$ were measured on a Bruker DPX-200 spectrometer at 200 MHz, using tetramethylsilane as an external standard.

Mass spectra were obtained on a Finnigan MATINCOS 50 quadrupole mass spectrometer (direct insertion, 70-eV electron impact ionization) and a PerkinElmer Model Clarus 500 gas chromatograph/mass spectrometer (SE-30 column).

Chromatographic analyses were carried out using LHM-2000 (1-m-long column, 3% Dexsil 300–Chrom W-AW) and Kristallyuks-4000M (ZB-1 column (Zebron) 100 m in length) chromatographs.

Thermogravimetric analysis (TGA) was performed in the range 50–950°C using a PerkinElmer Model PYRIS 6 TGA thermoanalytical system.

X-ray microanalysis was carried out on a Carl Zeiss NVision 40 scanning electron microscope (SEM) equipped with an Oxford Instruments X-Max detector and operated at an accelerating voltage of 20 kV.

Table 1. Specific surface area and crystallite size of the SnO_2/F catalyst

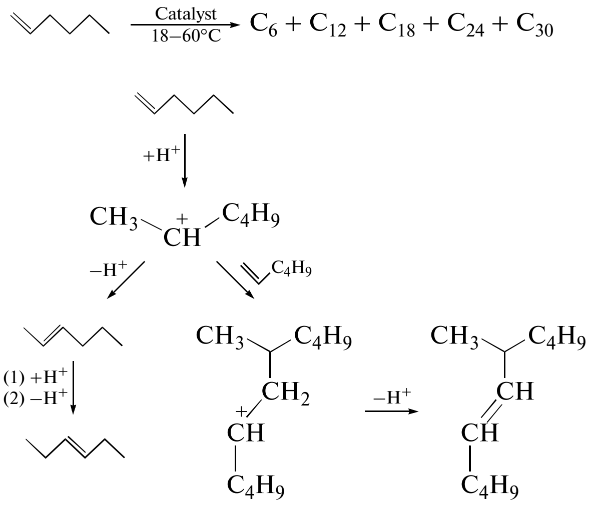
Heat treatment temperature, °C	Specific surface area, m^2/g	Crystallite size, nm
120	49	≈2
600	69	7

Catalyst synthesis. $SnCl_4 \cdot 5H_2O$ (50 g, 0.14 mol) was dissolved in water (300 mL) and then 30% aqueous ammonia was added dropwise with stirring until pH 10 was reached. The precipitate was washed with water until the test for chloride was negative, and dried at 120°C for 2 h. After cooling, a weighed amount (4 g) of the powder was added to 100 mL of an aqueous 2M NH_4F solution and the suspension was stirred for 1 h. The product was filtered off and dried at 120°C for 2 h.

1-Hexene oligomerization. Prior to catalytic experiments, the as-prepared catalyst was calcined at 600°C in flowing dry air for 2 h and then cooled in a dry atmosphere.

Catalytic activity was assessed as follows: The catalyst (1 g) was placed in a water-cooled flask, 1-hexene (0.04 mol, 3.4 g, 5 mL) was added, and the mixture was stirred at constant temperature. Samples of the reaction mixture (0.2 mL) were taken at intervals for analysis by NMR spectroscopy and chromatography. The degree of conversion of the starting compound was evaluated from ^1H NMR spectra, and the oligomer content was determined by gas–liquid chromatography (GLC).

Thermal desorption of pyridine. Catalyst samples (0.1 g) were calcined in dry air in a tubular reactor at 600°C. The temperature in the reactor was then lowered to 150°C, and the catalyst sample was exposed to flowing dry air, which had been bubbled through pyridine (1 mL) until it completely vaporized.



1-Hexene oligomerization.

Pyridine-saturated samples weighing 30 to 40 mg were placed in an alundum crucible under a dry pure argon atmosphere, and the crucible was then heated at a rate of 5°C/min in the range 50–950°C. The deviation of the reading of the thermobalance from zero was within ±0.025 mg in the range 50–950°C and less than ±0.01 mg in the range 300–700°C.

Catalyst acidity determination. The surface acidity of the catalyst was determined by visually assessing changes in the color of Hammett indicators [8]. A weighed amount (0.2 g) of the starting catalyst was first calcined at a temperature of 600°C and then cooled in flowing dry air. A weighed amount (0.2 mg) of an indicator (4-nitrochlorobenzene, 2,4-dinitrotoluene, 2,4,6-trinitrotoluene) was dissolved in sulfuryl chloride (2 mL) prepurified by distillation. Next, the indicator solution was added to the cooled catalyst, the suspension was shaken for some time, and we visually determined whether the color of the catalyst surface changed (from white to yellow).

RESULTS AND DISCUSSION

Physicochemical characterization of the catalyst. Determination of the strength of acid centers (Hammett acidity function H_0) on the samples showed that the acidity (H_0) of the catalyst obtained exceeded −16.04 (2,4,6-trinitrotoluene as an indicator).

This estimate indicates that SnO_2/F is a superacid according to Olah's definition ($H_0 \leq -11.93$ [9]).

The total density of acid centers on the catalyst surface, determined using thermal desorption of pyridine, was 0.09 mg-equiv/g.

The types of acid centers present on the surface of the fluorinated SnO_2 were identified by IR spectroscopy of adsorbed pyridine. Comparison of the present IR spectra of adsorbed pyridine and spectra reported previously clearly indicates that the surface of fluorinated tin dioxide has both Lewis and Brönsted acid centers [3].

The total fluorine content of the samples was determined by X-ray microanalysis. Heat treatment (600°C) was shown to reduce the mole fraction of fluorine by about a factor of 2 relative to the as-prepared material. In particular, the Sn/F molar ratio was ≃4 in the as-prepared material and ≃9 after annealing.

According to X-ray diffraction data, all of the fluorinated tin dioxide samples consisted of single-phase cassiterite (PDF no. 41-1445), with no impurity phases. Their diffraction peaks were strongly broadened, suggesting a small particle size of the fluorinated tin dioxide. Using the Scherrer formula, the crystallite size of the SnO_2 was estimated at ≃2 nm in the as-pre-

Table 2. Results of 1-hexene oligomerization by fluorinated tin dioxide, SnO_2/F, annealed at 600°C

Reaction time, h	Reaction temperature, °C	Percent conversion	Percent of C_{6-30}				
			C_6	C_{12}	C_{18}	C_{24}	C_{30}
2	18	20	–	–	–	–	–
24	18	30	74	15	10	1	0
1	40	31	70	17	12	1	0
1	60	31	65	19	13	3	0

pared material and 7 nm in the material heat-treated at a temperature of 600°C for 2 h (Table 1).

The specific surface areas of the powder before and after annealing at 600°C were 49 and 69 m^2/g, respectively (Table 1), as determined by low-temperature nitrogen adsorption measurements. From these data, the particle sizes were estimated at 17 nm in the as-prepared material and 12 nm in the annealed material. That the particle size evaluated from the low-temperature nitrogen adsorption data considerably exceeds that inferred from the X-ray diffraction data suggests that the particles were aggregated to a significant degree. The observed increase in specific surface area upon heat treatment was obviously due to the reduction in the degree of aggregation of the powder particles.

1-Hexene oligomerization. 1-Hexene was oligomerized in the presence of fluorinated tin dioxide at temperatures from 18 to 60°C. According to our results, the reaction proceeded along two paths: (1) migration of the terminal double bond, leading to the formation of 2-hexene and 3-hexene, and (2) 1-hexene oligomerization, leading to the formation of oligomers (Table 1). The general schemes and possible products of the corresponding reactions are shown in the figure.

The hexene-1 oligomerization products were characterized by GLC, gas chromatography/mass spectrometry, and ^1H NMR spectroscopy through comparison of the signal of the $CH_2{=}CH{-}R$ group in the parent 1-hexene to that of the $R{-}CH{=}CH{-}R'$ group in the reaction products (Table 2).

It is seen from the data in Table 2 that the degree of conversion of 1-hexene in 24 h is 30% at room temperature and varies little as the temperature is raised to 60°C. Chromatographic analysis data for the reaction mixture demonstrate that, with increasing reaction temperature, the C_6 content decreases slightly and, accordingly, the C_{12} and C_{18} contents increase. It is worth pointing out that the sulfated tin dioxide synthesized previously showed a higher catalytic activity for 1-hexene oligomerization [3] in comparison with the fluorinated tin dioxide. In the case of SnO_2/SO_4, the degree of conversion was 100% in 24 h at room temperature.

CONCLUSIONS

It is shown that nanocrystalline fluorinated tin dioxide is a superacid catalyst and promotes 1-hexene oligomerization and dimerization reactions.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, grant nos. 11-03-00981.

REFERENCES

1. Corma, A., Inorganic solid acids and their use in acid-catalyzed hydrocarbon reactions, *Chem. Rev.*, 1995, vol. 95, pp. 559–614.
2. Brown, A.S.C. and Hargreaves, J.S.J., Sulfated metal oxides—superactivity through “superacidity?”, *Green Chem.*, 1999, vol. 1, no. 1, pp. 17–20.
3. Yurkova, L.L., Lermontov, S.A., Kazachenko, V.P., et al., Sulfated SnO_2 as a high-performance catalyst for alkene oligomerization, *Inorg. Mater.*, 2012, vol. 48, no. 10, pp. 1012–1019.
4. Cai, T., Studies of a new alkene oligomerization catalyst derived from nickel sulfate, *Catal. Today*, 1999, vol. 51, pp. 153–160.
5. Cai, T., Zang, L., Qi, A., et al., Propene oligomerization catalyst derived from nickel sulfate supported on γ-alumina, *Appl. Catal.*, 1991, vol. 69, pp. 1–13.
6. Lermontov, S.A., Yurkova, L.L., Malkova, A.N., et al., Fluorinated metal oxide-assisted oligomerization of olefins, *Mendeleev Commun.*, 2013, vol. 23, pp. 110–112.
7. Andersson, A., Johansson, N., Broms, P., et al., Fluorine tin oxide as an alternative to indium tin oxide in polymer LEDs, *Adv. Mater.*, 1998, vol. 10, pp. 859–863.
8. Tanabe, K., *Solid Acids and Bases: Their Catalytic Properties*, New York: Academic, 1970.
9. Olah, G.A., Prakash, G.K., and Sommer, J., Superacids, *Science,* 1979, vol. 206, pp. 13–20.

Translated by O. Tsarev