Sulfated SnO₂ As a High-Performance Catalyst for Alkene Oligomerization


Abstract—Nanoparticulate (3–5 nm) sulfated tin dioxide shows high catalytic activity for the oligomerization of isobutylene, hexene-1, and cyclohexene. The acidity (Hammett acidity function $H_0$) of sulfated stannia reaches $H_0 = -16.04$. We have studied the effect of synthesis conditions on the physicochemical and functional properties of sulfated SnO₂.

DOI: 10.1134/S0020168512100147

INTRODUCTION

Sulfated metal oxides possessing highly acidic properties are an environmentally safe alternative to sulfuric acid, which is widely used in industrial processes [1, 2]. The acidity of sulfated oxides depends on many parameters: the nature of the metal, oxide preparation procedure, sulfation method, calcination temperature, particle size, and surface area [3].

Sulfated zirconium and tin dioxides are thought to have large Hammett acidity functions ($H_0$) compared to other sulfated oxides, for example TiO₂, Fe₂O₃, and Al₂O₃ [1]. In particular, Arata et al. [4] determined the $H_0$ of sulfated ZrO₂ and SnO₂ to be -16.1 and -18.0, respectively. As shown in detailed studies of acid centers in sulfated ZrO₂ and SnO₂ using temperature-programmed ammonia desorption [5], sulfated tin dioxide contains a smaller amount of strong acid centers (14%) than does sulfated zirconium dioxide (42%), but their relative strength is far higher.

Sulfated tin dioxide is successfully used in laboratory applications as a catalyst for many reactions, including hydrocarbon isomerization [6, 7], heptane polymerization [8], alkane alkylation [9, 10] and oxidation [11, 12], phenol methylation [13], Friedel–Crafts acylation, etherification and esterification [5, 14–18], and some other processes [19–22].

Oligomerization of alkenes catalyzed by sulfated tin dioxide has not yet been investigated. At the same time, isobutylene oligomerization on sulfated ZrO₂ and SnO₂ under pressure at room temperature has been the subject of several studies [23–25].

The purpose of this work is to analyze the influence of synthesis conditions on the physicochemical properties of sulfated nanocrystalline tin dioxide and its catalytic activity for the oligomerization of alkenes (isobutylene, hexene-1, and cyclohexene).

EXPERIMENTAL

Catalyst synthesis. SnCl₄ ⋅ 5H₂O (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, the powder was thoroughly ground and treated with a sulfuric acid solution (0.3 M or 3 M) for 1 h on a magnetic stirrer (30 mL of the H₂SO₄ solution for 2 g of Sn(OH)₄). The precipitate was then dried at 120°C for 5 h.

The phase composition of the solid samples was determined by X-ray diffraction on a Rigaku D/MAX 2500 diffractometer (CuKα radiation, 20 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 nitrogen for 30 min. The specific surface of the powders was evaluated using Brunauer–Emmett–Teller (BET) analysis (six points).

$^1$H and $^{13}$C NMR spectra in CDCl₃ were measured on a Bruker DPX-200 spectrometer at 200 and 50.3 MHz, respectively, using tetramethylsilane as an external standard.

Mass spectra were obtained on a Finnigan MAT-INCOS 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 LKhM-2000 (1-m-long column, 3% Dexsil 300–Chrom W-AW) and Kristallyuks-4000M (ZB-1 column (Zebron) 100-m long) chromatographs.

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

**Oligomerization of alkenes.** Prior to experiments, the catalyst was calcined at 400–600°C in flowing dry air for 2 h and then cooled in a dry atmosphere.

Next, the catalyst (1 g) was placed in a water-cooled flask, an alkene (0.1 mol) was added, and the mixture was agitated on a magnetic stirrer 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 alkene was evaluated from $^1$H NMR spectra.

A cyclohexene dimer was isolated by distillation ($t_b = 150$°C).

Isobutylene was oligomerized as described elsewhere [26].

**Thermal desorption of pyridine.** Catalyst samples (0.1 g) were calcined in dry air in a tubular reactor at 400, 500, and 600°C. The temperature in the reactor was then lowered to 150°C, and the catalyst sample was exposed to flowing dry air, which was bubbled through pyridine (1 mL) until it completely vaporized. Samples weighing 30 to 40 mg were placed in an aluminuocrucible under a dry pure argon atmosphere. The heating rate in the range 390–460°C was 5°C/min. 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.

**RESULTS AND DISCUSSION**

**Isobutylene oligomerization.** The isobutylene oligomerization process is of practical interest because the resulting isooctenes are easy to hydrogenate to isooctane, which is one of the most important and environmentally safe components of modern gasolines. We attempted to synthesize isobutylene oligomers at different temperatures in the range 18–180°C with solid acids without pressure (Fig. 1).

We used two types of catalysts: tin dioxide treated with 0.3 M and 3 M sulfuric acid solutions (catalysts I and II, respectively). The results are summarized in Table 1. It is seen that, at 18°C (run 1), the fraction of C₈ isomers was small: on the order of 2%. At 120°C, the sum content of C₈ and C₁₂ reached 96%, with C₈ : C₁₂ = 1 : 1 (run 2). Running the reaction at 150°C increased the content of C₈ + C₁₂ oligomers to 98–99%, with C₈ : C₁₂ = 3 : 2 (run 3). Raising the temperature to 180°C increased the C₈ content to 73%, whereas the C₁₆ content was very low (run 4). At 210°C, the reaction ceased (run 5), probably because of the resification of the organic compounds on the surface of the catalyst.

Calcination of the catalysts at other temperatures (500 and 400°C) had no significant effect on the composition or yield of the reaction products (runs 8 and 9).

To examine the effect of water on the isobutylene oligomerization reaction, isobutylene was initially passed through water in a bottle (run 6). The presence of water vapor at a reaction temperature of 150°C had no effect on the composition of the reaction products.

The catalysts can easily be regenerated by recalcining them in flowing dry air, and the calcined catalyst does not lose its activity (run 7).

The present results lead us to conclude that, by varying the temperature of the catalytic reaction, one can tune the relative amounts of C₈, C₁₂, and C₁₆ in the reaction mixture. The observed regular trends—the increase in the percentage of C₈ dimers and reduction in the percentages of C₁₂ trimers and C₁₆ tetramers with increasing reaction temperature—can be accounted for by the fact that, when isobutylene passes through a catalyst at low temperatures, the liquid reaction products are partially retained on the catalyst surface and react with the alkene being fed, leading to the formation of heavier fractions. Raising the reaction temperature to above the boiling point of the reaction