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SULFATED NANO-CERIA AS A CATALYST OF HEX-1-ENE OLIGOMERIZATION

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Oligomerization of hex-1-ene over acid catalysts obtained by the impregnation of cerium dioxide by sulfate-containing compounds (sulfuric acid or its salts) was studied. Maximum conversion of hexene-1 over sulfated ceria catalysts was 7–12% at 60 ° C.

Keywords: sulfated ceria, olefins oligomerization, hex-1-ene.

1. Introduction

Traditional acid-catalyzed industrial processes are often criticized because strong mineral acids are used as catalysts. The low cost of these catalysts does not compensate for the costs associated with the production of corrosion-resistant equipment, the transportation and disposal of liquid acid wastes. To solve this problem, sulfated metal oxides, possessing highly acidic properties were developed as an environmentally-safe alternative to mineral acids [1,2]. Superacidic catalysts based on fluorinated oxides are also known [3].

Solid acids including sulfated titania, zirconia, and stannia are among the most promising heterogeneous catalysts [4]. The acidity of sulfated oxides depends on many parameters, such as the nature of the metal, oxide preparation procedure, sulfation method, calcination temperature, particle size, and surface area [4]. Their acidity is much higher than that of concentrated H_2SO_4, with their surface sulfate groups promoting the formation of Lewis and Brønsted acid sites [5]. The Hammett acidity functions H_0 for SO_4/ZrO_2 and SO_4/SnO_2 range from –16 to –18; while SO_4/TiO_2 has a slightly lower value of –14.6 [6]. The SO_4/ZrO_2 is the most comprehensively studied system, because its acidity is one of the highest among the sulfated oxides [5,7–12]. The main advantages of solid acid oxide catalysts include high stability at elevated temperatures, resistance to deactivation and easy regeneration.

Cerium dioxide (CeO_2) is a multifunctional inorganic compound holding a great promise for a wide range of technological applications, including catalysis, ultraviolet shielding materials, sensors, electrochromic devices, anticorrosion coatings, abrasive materials, etc.

Cerium dioxide is widely used in redox catalysis and as an effective antioxidant [13]. Recently, cerium dioxide-based catalysts, wherein CeO_2 acts as a so-called oxygen buffer, has been widely used. The relative ease of $Ce^{4+} \leftrightarrow Ce^{3+}$ transition in CeO_2 makes it possible to accumulate and release oxygen depending on the O_2 content in the environment —

cerium dioxide can accumulate oxygen from oxygen-enriched mixtures and, in the presence of reducing agent, release it forming nonstoichiometric CeO_{2-x} [14].

Despite the considerable information on CeO_2 catalytic systems, CeO_2 has not been studied yet as a solid acid. In this paper, we present the first use of sulfated cerium dioxide (CeO_2/SO_4) as a solid acid for hex-1-ene oligomerization. Hex-1-ene was chosen as a model long-chain terminal olefin in the oligomerization reaction catalyzed by modified ceruim dioxide. Previously, hex-1-ene oligomerization was used to probe the catalytic activity of both sulfated zirconia [15] and sulfated stannia [16].

2. Experimental

2.1. Catalysts synthesis

All starting materials used in the experiments were of analytical grade.

Ceria nanopowders were synthesized using a previously-described method [17]. A solution of $Ce(NO_3)_3 \cdot 6H_2O$ (0.08 mol L^{-1}) in water/isopropanol mixture (1:1 v/v) was rapidly added under vigorous stirring to an aqueous ammonia (3 mol L^{-1}) solution taken in a five-fold molar excess. The resulting mixture was allowed to stir for 3 h at room temperature. Then, a yellow precipitate was separated by centrifugation, thoroughly washed by distilled water and then dried in air at 50 °C.

To prepare each catalyst, 4 g of ceria nanopowder and 100 mL of aqueous 2M NH_4F, or 1M $(NH_4)_2SO_4$, or 0.3M H_2SO_4, or 3M H_2SO_4 were stirred for 1 h in a glass flask at room temperature, filtered and dried at 100 °C.

2.2. Methods

IR spectroscopy was performed on a Spectrum One (Perkin Elmer, USA) spectrometer from the 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 ($\sim$ 0.04 g) was calcined in a dry air flow tube reactor at 475 °C. After that, the temperature was decreased to 150 °C, a bubbler with 1 mL of pyridine was embedded into an air line and a resulting gas-pyridine mixture was passed over the catalyst sample until all pyridine was evaporated.

Low temperature nitrogen adsorption measurements were conducted using an ATX-6 analyzer (Katakon, Russia). Before measurement the samples were outgassed at 200 °C for 30 min under dry helium flow. Surface area determination was carried out by the 8-point Brunauer-Emmett-Teller (BET) method.

Powder X-ray diffraction (XRD) analysis was carried out on a Rigaku D/Max 2500 diffractometer (CuKα radiation) with a rotating copper anode ($Cu_{K\alpha}$ irradiation, 5–80 ° 2θ range, 0.02 ° step). Particle size was estimated using the Scherrer equation. Diffraction maxima were indexed using the PDF2 database.

Transmission electron microscopy images were taken using Leo 912 AB Omega electron microscope operating at 100 kV. Microstructure of the samples was also studied using a Carl Zeiss NVision 40 scanning electron microscope (micrographs were obtained at 1 kV acceleration voltage) equipped with Oxford Instruments X-MAX energy-dispersive X-ray (EDX) analyzer operating at 20 kV acceleration voltage. The samples were not specially prepared (*e.g.* coated with conducting material) for TEM and SEM measurements. Before EDX analysis the samples were coated with $\sim$5 nm Au/Pd.

NMR spectra were recorded using a Bruker DPX-200 spectrometer in $CDCl_3$. Tetramethylsilane (TMS) was used as an external standard.

2.3. Hex-1-ene oligomerization

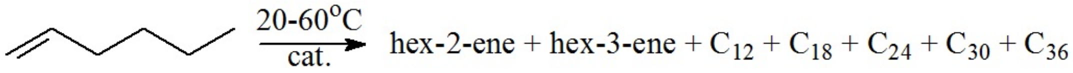
1 g of a catalyst sample was pre-conditioned in air at a chosen temperature (400, 475, or 500 ° C) for 2 h in air and then cooled in a dry atmosphere.

A catalyst (1 g) and 0.1 mol of hex-1-ene were then placed into a water-jacketed glass flask and kept at constant temperature (20–60 ° C) under vigorous stirring. Samples of the reaction mixture were periodically taken for ^{1}H-NMR and GC-MS analysis. A conversion degree was determined by monitoring the disappearance of vinyl group protons disappearance *via* ^{1}H-NMR.

3. Results and discussion

3.1. Hex-1-ene oligomerization

We found that sulfated ceria acts as an acid catalyst causing hex-1-ene oligomerization at moderate temperatures:



Catalytic activity of sulfated ceria samples depended strongly on the method of their preparation and the pre-conditioning temperature. The results of catalytic experiments are presented in Table 1.

TABLE 1. Hex-1-ene oligomerization

Entry	Reaction time, h	Reaction temperature, ° C	Calcination temperature, ° C	Catalyst	Conversion, %
1	24	rt	400	0.3M H_2SO_4/CeO_2	0-2
2	2	rt			0-2
3	1	40			0-2
4	1	60			7
5	1	60	400	3M H_2SO_4/CeO_2	2
6	1	60	500	0.3M H_2SO_4/CeO_2	2
7	24	rt	475	1M $(NH_4)_2SO_4/CeO_2$	0
8	1	40			2
9	1	60			12
10	24	rt-60	475	2M NH_4F/CeO_2	0-2
11	1	60	475	CeO_2	0

Olefin isomerization and oligomerization are acid-catalyzed processes which were initiated by proton addition to a C=C bond (Fig. 1) to yield a secondary carbocation. This intermediate may then add to another molecule of hex-1-ene, yielding the dimeric carbocation shown, or, the initial intermediate may eliminate an H^+ to yield the isomerized internal alkene.

Highly acidic conditions are necessary for this process: ZrO_2 ($-3.0 < H_0 < +1.5$ [18]) and TiO_2 ($H_0 \leq -3.0$ [19]) showed no catalytic effect in olefin oligomerization. Table 1 shows that sulfated ceria samples acquire acidic properties which are not inherent to unmodified CeO_2. The 1M $(NH_4)_2SO_4/CeO_2$ catalyst appeared to be slightly more active than the 0.3M H_2SO_4/CeO_2 and 3M H_2SO_4/CeO_2. A sample calcined at 500 ° C was relatively inactive.

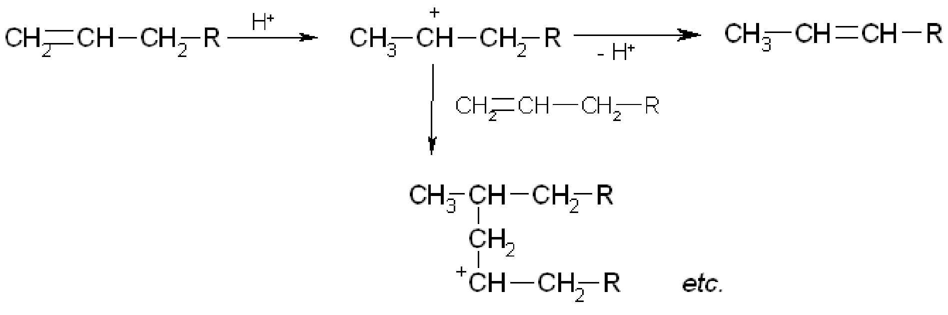


FIG. 1. Scheme of hex-1-ene oligomerization

Recently, we showed that fluorinated alumina is highly acidic ($-13.75 < H_0 < -12.7$) and have postulated that fluorination, instead of sulfation, might be used for solid superacid preparation [3], but, surprisingly, fluorinated ceria was practically inactive as an acid catalyst in this reaction (entry 10).

3.2. Physical and chemical properties of sulfated ceria

The specific surface area of the most active 1M $(NH_4)_2SO_4/CeO_2$ sample calcined at 475 ° C was 75 m^2/g and did not differ significantly from that of untreated ceria (79 m^2/g).

XRD studies have indicated that only CeO_2 phase is present in both samples and that the average particle size, as estimated using the Scherrer equation, was 6.7–6.9 nm. These data were also confirmed by transmission electron microscopy (Fm–3m, PDF #34-394). Both of the samples (sulfated and unmodified ceria) were highly aggregated powders, consisting of nearly monodisperse particles ~7 nm in size. Note that particle size in starting CeO_2 powders prepared by precipitation from water/alcohol solutions was about 4.5 nm. Thus, heating of starting materials at 475 ° C resulted in an increase in the particle size, which is in line with our previous studies of ceria nanopowders (for example, see [20]).

EDX analysis revealed the presence of ~ 4 at % sulfur on the surface of sulfated samples prepared by pre-conditioning of sulfated ceria at 475 ° C.

We could not estimate the H_0 value for sulfated ceria using relevant organic indicators because of the intensive yellow color of the samples. To determine the types of acidic centers of the 1M $(NH_4)_2SO_4/CeO_2$ catalyst, we used IR spectroscopy data from the pyridine adsorbed onto the surface of the powders. The IR spectra of sulfated ceria samples calcined at 475 C contained bands which were characteristic for pyridinium ions adsorbed on both Lewis (L) and Bronsted (B) acid centers (cm^{-1}) 1445 (L); 1490 (B+L); 1540 (B); 1639 (L) [21, 22] (Fig. 2).

4. Conclusions

In this paper, we have shown that nanocrystalline sulfated CeO_2 possesses acidic properties and demonstrated that it acts as an acid catalyst and promotes the oligomerization and isomerization of hex-1-ene.

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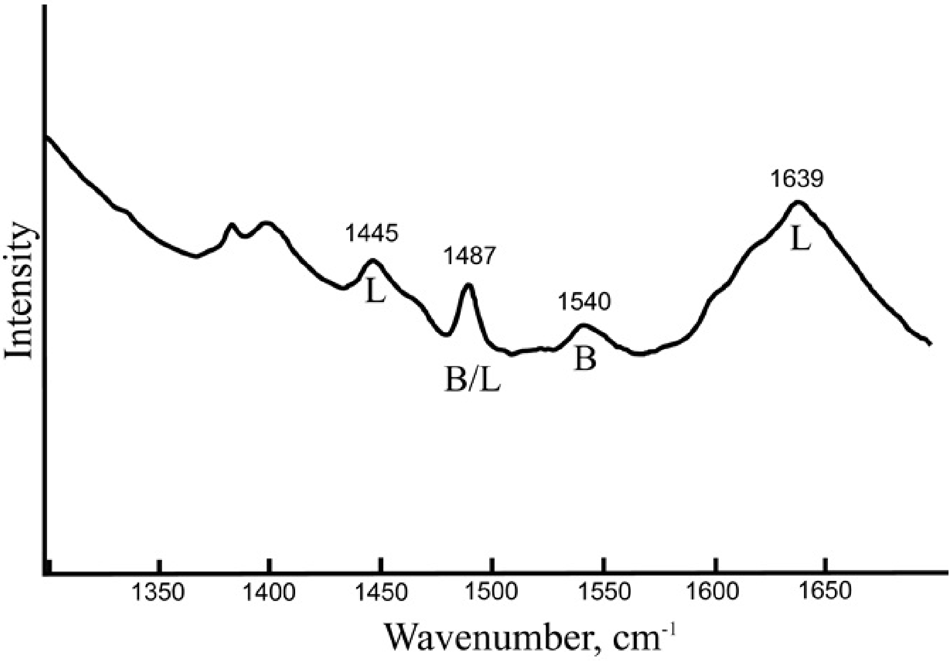

FIG. 2. IR spectroscopy data of pyridine adsorbed onto the surface of the 0.3M H_2SO_4/CeO_2 and 1M $(NH_4)_2SO_4/CeO_2$ catalyst

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