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Sulfated zirconia-catalyzed alkylation of phenol with camphene and isomerization of *n*-butane

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Sulfated zirconia modified with polyvalent cations is capable of catalyzing alkylation of phenol with camphene and isomerization of n-butane into isobutane.

Development of catalysts and processes for alkylation of phenols is an important problem since such products find use in medicine and other areas. Terpenophenols are among the most demanded compounds for their antioxidant and pharmacological activity.^{1,2} Synthesis of terpenophenols is based on catalytic alkylation using acid catalysts, such as mineral or organic acids, metal halides, cation-exchange resins, solid oxides *etc.*^{3–8} Some aluminumcontaining organoelement compounds providing high selectivity of *ortho*-alkylation of phenols can be used as homogeneous catalysts.^{3,6,9}

Sulfated oxides are known^{10,11} to exhibit strong acidic properties exceeding the acidity of zeolites. For instance, sulfated zirconium dioxide is sometimes classified as a solid superacid.¹² The strength of acid sites in such systems increases in the range $Al_2O_3 < TiO_2 < ZrO_2$. Some multivalent metal ions (Fe, Mn, Ga, Zn, Co) are capable of enhancing the acidic properties of these solid acids,^{13–15} which is usually accounted for the inductive effect of the multivalent cation on the Brønsted acid sites, *i.e.*, OH groups bonded to the introduced sulfate moieties.

Sulfated oxides possess certain additional benefits compared to zeolites. As a rule, the range of the catalytic applications of zeolites is limited by the diameter of zeolite entrances (< 0.65 nm) and cavities (< 1.3 nm), which would restrict the size of the interacting molecules, typically below 1 nm. For the sulfated oxides based on rather wide-pore carriers (ZrO₂, TiO₂, Al₂O₃), such limitations are absent. Furthemore, the sulfated systems are characterized by the enhanced thermal stability, as far as they are typically prepared by calcinations at temperatures higher than 650 °C.

This work is focused on the study of the alkylation of phenol with camphene in the presence of sulfated catalysts based on zirconium dioxide,[†] including the systems modified with cations of gallium, iron, cerium and vanadium. These catalysts were also tested in isomerization of *n*-butane, a reaction requiring the presence of very strong Brønsted acid sites.



Figure 1 IR spectra of 5% SO $_4^{2-}$ /ZrO $_2$ calcined in air at (1) 650, (1) 750 and (3) 850 °C.

IR spectra of the samples of sulfated zirconia in the region of OH group stretching vibrations (4000–3500 cm⁻¹) are presented in Figure 1. The spectra represent a superposition of the narrow absorption bands with maxima at 3730 and 3640 cm⁻¹ attributed to terminal and bridging ZrOH groups, respectively.

In addition to the narrow lines, a broad absorption band of the main stretching OH vibrations at 3350–3150 cm⁻¹ is also observed with its maximum and intensity being dependent upon the pretreatment temperature in the range of 650–850 °C. Earlier⁹ this band was ascribed to the delocalized protons emerged from H₂SO₄. These protons can also be shared with oxygen atoms of the zirconia framework (Figure 2). The IR spectra of the SO²₄-/ZrO₂ catalysts additionally modified with metal ions are very similar to the spectrum of the unmodified SO²₄-/ZrO₂ sample.

Isobornyl phenyl ether **3a** was found to be the main product of the alkylation of phenol **1** with camphene **2** (Scheme 1).[‡] C-Alkylated phenols, namely 2-isobornylphenol **4a** and 2-isocamphylphenol **4b** were formed in minor quantities (Table 1). The

[†] ZrO₂ was prepared by calcination of Zr(OH)₄ ($S_{surf} = 150 \text{ m}^2 \text{ g}^{-1}$, Magnesium Electron Co., grade XZO632/03) at 500 °C for 2 h in a flow of air. In order to prepare SO₄²/ZrO₂, SO₄²⁻ anions were introduced from a 1 M aqueous solution of H₂SO₄; the concentration of sulfate groups in the samples was 5 wt%. The samples were dried at 120 °C for 6 h and calcined in a flow of dry air at 650 °C for 2 h. Modification with metal cations was carried out by incipient wetness impregnation of the calcined sulfated sample with 0.3 M aqueous solutions of Fe³⁺, Ga³⁺, Co³⁺, Ce³⁺,

 VO^{2+} nitrates with further drying at 120 °C for 6 h and calcinations in a flow of dry air at 650 °C for 2 h. The loading of the modifying metal was 2 wt%.

Prior to spectral studies, the samples were calcined at 300–650 °C in a vacuum for 2 h in a quartz IR-ampule supplied with a CaF₂ window. Diffuse-reflectance IR spectra were measured with a Nicolet Impact 410 FTIR spectrometer and processed using the Kubelka–Munk function (the OMNIC program).



Figure 2 Delocalized protons in sulfated zirconia.

Table 1 Sulfated zirconia-catalyzed alkylation of phenol with camphene.

Catalyst	T/°C	t/h	Phenol conver- sion (%)	Product composition (%)		
				3a	3b	4a + 4b
2Fe ³⁺ /5SO ₄ ²⁻ /ZrO ₂	60	3	76	71	11	18
2Ga ³⁺ /5SO ₄ ²⁻ /ZrO ₂	100	3	84	92	5	3
2Ce ³⁺ /5SO ₄ ²⁻ /ZrO ₂	100	5	70	79	9	12
2V ⁵⁺ /5SO ₄ ²⁻ /ZrO ₂	110	3	0	_		_
ОН	OH M-			OR		ОН



Scheme 1

content of **3a** was 70%, whereas in the case of the Ga-modified catalyst it reached 92%. The catalysts can be ranked in terms of the activity in phenol alkylation with camphene as follows: $2Fe^{3+}/5SO_4^2/ZrO_2 > 2Ga^{3+}/5SO_4^2/ZrO_2 > 2Ce^{3+}/5SO_4^2/ZrO_2 > 2V^{5+}/5SO_4^2/ZrO_2$. Note that the Fe-containing catalyst demonstrates a very high conversion of phenol already at 60 °C.

A similar case of the catalyst activity was revealed for isomerization of *n*-butane into isobutane[§] (Figure 3). The yield of isobutane was as high as 30%, which is close to the thermodynamic equilibrium (~40% at 190 °C). Vanadium-containing catalyst turned out to be inactive in both reactions. This can result from the poisoning effect of vanadium on Brønsted acid sites that are responsible for alkylation and isomerization.

In conclusion, some sulfated oxide catalysts possess high activity in alkylation and isomerization at rather low temperatures. Note that, for comparison, acidic forms of zeolites cause isomerization of *n*-butane only at temperatures above $240 \,^{\circ}$ C, and only chlorinated alumina, an environmentally unfriendly



Figure 3 Yield of isobutane in the course of *n*-butane isomerization on sulfated zirconia and that modified with metal cations (190 °C, liquid hourly speed velocity is 1 h^{-1}).

commercial catalyst for isomerization of *n*-butane, is active at lower temperatures (140–160 °C) than those found for the sulfated zirconia (~190 °C). Sulfated oxides are also promising for other acid-catalyzed chemical processes.

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[‡] Phenol and camphene were taken in a molar ratio 1:1, the reaction was carried out by stirring the mixture at 100 °C for 3–5 h in the presence of a catalyst. ¹H and ¹³C NMR spectra of the products were obtained using a Bruker Avance II 300 spectrometer (300 and 75 MHz, respectively) in CDCl₃ at room temperature. Chloroform was used as an internal standard ($\delta_{\rm H}$ 7.26 ppm, $\delta_{\rm C}$ 76.90 ppm). Assignment of signals was made using ¹³C NMR spectra measured in the JMOD regime. Analysis of volatile products was performed by GC with a Shimadzu GC-2010AF chromatograph with a flame-ionization detector (He as a carrier gas) using an HP-1 capillary column (Agilent, 60 m×0.25 mm×0.25 µm, temperature range 100–240 °C, heating rate 6 K min⁻¹).

 $^{^{\$}}$ Isomerization of *n*-butane was studied in a flow reactor at 190 °C, pressure of 1 atm, butane liquid hourly space velocity 1 h⁻¹. Products were analyzed by GC.