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Synthesis and study of acid catalyst 30% WO_3/SnO_2

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Abstract

Solid acid catalyst 30% WO_3/SnO_2 was synthesized and studied by IR, X-ray powder diffraction, solid state ^{117}Sn NMR and adsorbed pyridine thermodesorption. The catalyst consists of SnO_2 grains covered with W(VI) octahedra organized as in heteropolyacids. Its acidity is lower than the acidity of heteropolyacids but higher than that of the analogous catalyst WO_3/ZrO_2. The catalyst exhibits a high activity when used in the liquid phase acid-catalyzed reactions, but a part of it is washed out by polar solvents or substrates. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Catalysts consisting of 10–45 wt.% WO_3 supported on ZrO_2, SnO_2, etc., are solid acids actively investigated and used in acid-type catalysis during the last years ([1–5] and references therein). These catalysts are usually prepared by impregnating Zr or Sn hydroxide with $(NH_4)_6H_2W_{12}O_{40}$ solution followed by calcination at 600–1000°C. Materials containing 11–20% $WO_3/(ZrO_2$ or $SnO_2)$, calcined at 800–850°C possess the highest acidity and surface area of 30–60 m^2/g. There is a variety of works focused on the studies of WO_3/ZrO_2, but only one work concerning WO_3/SnO_2 [1]. Here, we report the synthesis and study of the solid acid catalyst 30 wt.% WO_3/SnO_2.

2. Experimental

Unlike the usual method [1–5], we have synthesized the WO_3/SnO_2 catalyst starting from homogeneous aqueous solutions containing Sn(IV) and W(VI). $SnCl_2 + H_2O_2$, $SnSO_4 + H_2O_2$, H_2SnO_3 were used as sources of Sn(IV). Heteropolyacids $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$, peroxometatungstate acid $H_6H_2W_{12}O_{40-x}(O_2)_x$ (prepared by electrodialysis of Na_2WO_4 solution in the presence of H_2O_2 by method similar to that for heteropolyacids [6]), $(NH_4)_6H_2W_{12}O_{40}$ were used as sources of W(VI). The solution was evaporated to dryness, the resulting solid was calcined in air. The materials for catalytic experiments were: tetrahydrofurane of polymerization grade, acetic anhydride (97%), L-sorbose (98%), acetone (99.5%), 2,3,5-trimethylhydroquinone (98%), isophytol (Rhone-Poulenc, 91%). For instrumental studies IR-spectrophotometer Specord 75IR, NMR-spec-
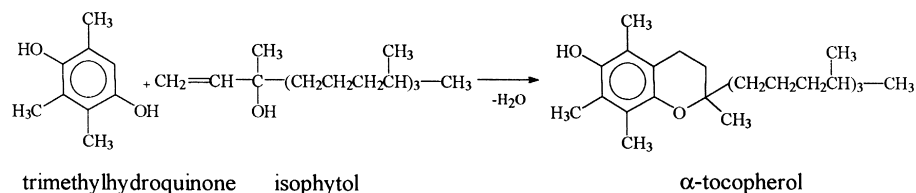
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Table 1

Yield of α-tocopherol with 30% WO_3/SnO_2. Loadings: 1.55 g trimethylhydroquinone, 3.25 g isophytol, 7 ml solvent, 0.46 g the catalyst. Reaction time 2 h

Solvent	Temperature (°C)	Yield of α-tocopherol by ^{13}C NMR
Isopropylacetate	90	9
Acetic acid	118	47
1,2-Dichloroethane	84	35
Toluene	90	–
Hexane	68	25
Heptane	98	76
Octane	145	81
Acetone	56	20
Gasoline	98	68

trimethylhydroquinone   isophytol   α-tocopherol

trometer Bruker MSL-400, XRD-spectrometer HZG-4C, derivatograph Q-1500D MOM were used.

For catalytic testing, three liquid phase reactions were carried out: (1) sorbose acetonation L-sorbose + acetone → 2,3-acetonesorbose → 2,3;4,6-diacetonesorbose (conditions as in Ref. [7], catalyst loading 0.75 g), (2) homopolymerization of tetrahydrofurane: tetrahydrofurane + H_2O or Ac_2O → polyTHF (60°C, 5 h, catalyst loading 30% on THF), (3) synthesis of α-tocopherol (vitamin E): trimethylhydroquinone + isophytol → α-tocopherol (see Table 1 for conditions).

3. Results and discussion

3.1. Synthesis and catalysis

Optimal conditions for the WO_3/SnO_2 catalyst were determined by catalytic testing in reaction (1). The best catalyst was 30% WO_3/SnO_2 prepared from $H_6H_2W_{12}O_{40-x}(O_2)_x$ and $SnCl_2 + H_2O_2$ and calcined at 800°C for 6–8 h.

$S = 70$ m^2/g. Similar properties were demonstrated by 50% WO_3/SnO_2 made from $H_6H_2W_{12}O_{40-x}(O_2)_x$ and $SnSO_4 + H_2O_2$, $S = 55$ m^2/g. Product yield was up to 92% of theoretical diacetonesorbose yield. However, according to ^{13}C NMR the product consisted of only 30% diacetonesorbose and 70% of monoacetonesorbose. Monoacetonesorbose produced was not the 2,3-isomer but, probably, the 1,2-isomer which can hardly be further acetonated. If the second step of reaction (1) was carried out, 2,3;4,6-diacetonesorbose with yield ~ 100% was produced. Thus, WO_3/SnO_2 catalyst showed its ability to catalyze liquid phase acid-catalyzed reactions, but step one in reaction (1) was nonselective.

Unlike in the case of heteropolyacid catalysts, with 30% WO_3/SnO_2, reaction (2) did not proceed in the presence of water. In the presence of Ac_2O, polytetramethyleneglycolediacetate was produced in 44% yield (thermodynamic maximum at 60°C) as with $HClO_4$ as catalyst. In reaction (3), the yield of the target product was up to 81% (Table 1). The catalyst can be regenerated by calcining in air after each experiment without loss of its activity.

3.2. Study of the catalyst 30% WO_3/SnO_2

The catalyst was studied by a number of methods. According to solid state [117]Sn NMR and X-ray powder diffraction, Sn existed as SnO_2 particles of average size ~ 10 nm, and W was not detected. There were some bands in the IR-spectrum at 700–1000 cm^{-1} (Fig. 1) which were very usual in the spectra of octahedral W(VI) constructing heteropolyacids. The catalyst was soluble a little up to 1.5% (of its initial weight) in water and 0.1% in polar solvents during catalytic reactions. Moreover, the soluble phase was enriched with W, and the IR-spectrum of this phase (Fig. 1) corresponded to one of the Keggin-type heteropolyacids such as $H_6H_2W_{12}O_{40}$ or $H_3PW_{12}O_{40}$, with SnO_2 admixture. On the whole, we have concluded that the catalyst 30% WO_3/SnO_2 consists of SnO_2 grains covered with WO_6 octahedra organized as in heteropolyacids, as have been found for the catalyst WO_3/ZrO_2 [2,3]. Such a structure may be responsible for the high acidity characteristic of heteropolyacids.

The acidity of the catalyst was not measured by indicator method because of brown-grey coloring. So we studied its acidity by thermoprogrammed desorption of pyridine adsorbed from benzene solution. There was the band at 1540 cm^{-1} in the IR-spectrum of adsorbed pyridine which indicated the Brönsted-type acid centres, and Lewis centres were not found. Under heating at the rate 10°/min, Py was removed up to 520°C. Two maxima at 415°C and 480°C appeared in the DTA curve. The amount of acid centres was 2.9 μmol/m^2. For comparison, pyridine was removed from 10–14% WO_3/ZrO_2 at 350–400°C [8], 18% WO_3/ZrO_2 possessed 1.9 μmol/m^2 of acid centres [4]. From heteropolyacid $H_3PW_{12}O_{40}$, adsorbed pyridine was removed up to 600°C, maxima at 475°C and 560°C appeared in the DTA curve. Thus, the catalyst 30% WO_3/SnO_2 is somewhat more acidic than WO_3/ZrO_2 but somewhat less acidic than $H_3PW_{12}O_{40}$.
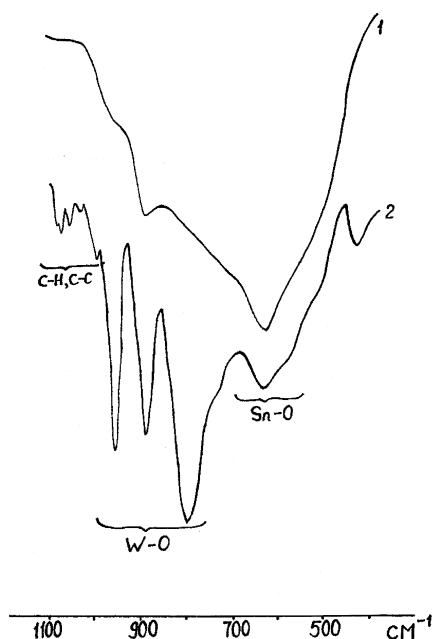
4. Conclusions

The reusable catalyst 30% WO_3/SnO_2 is a strong solid acid analogous to WO_3/ZrO_2. It consists of SnO_2 grains covered with heteropolyacid-like structure of W(VI) octahedra. The catalyst can be used in the gas or liquid phase acid-catalyzed reactions combining with nonpolar solvents not leaching heteropolyacids.

Acknowledgements

Fig. 1. IR spectra: 1 — 30% WO_3/SnO_2; 2 — tetrabutylammonium salt of water-soluble phase of the catalyst.

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