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WO_3/MO_2 (M = Zr, Sn, Ti) Heterogeneous Acid Catalysts: Synthesis, Study, and Use in Cumene Hydroperoxide Decomposition

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Abstract—Thirty (5–40)% WO_3/MO_2 (M = Zr, Ti, Sn), heterogeneous acidic catalysts have been synthesized by two methods, specifically, via homogeneous acid solutions and from solutions brought to pH 9 with ammonia, both followed by calcination at 600–900°C. The catalysts have been characterized by IR spectroscopy and scanning electron microscopy, and their aqueous washings have been analyzed. Their acidity has been determined by the thermal analysis of samples containing adsorbed pyridine, and in terms of the proton affinity scale. Catalytic activities have been compared for cumene hydroperoxide (CHP) decomposition at 40°C in cumene and acetone. For all M, the catalysts are one type and contain W in strongly and weakly bound states, the latter being a polyoxometalate that can be washed off. Both tungstate phases are active in acid catalysis. Brønsted acid sites with a broad strength distribution have been found. The strongest of them are heteropolyacid protons. The catalysts 30% WO_3/SnO_2 and 20% WO_3/ZrO_2 (in acetone) and 10–20% WO_3/TiO_2 (in cumene) are the most active in CHP decomposition, and their activity is not related to their total acidity. Phases containing W^{6+} that form during the high-temperature synthesis are responsible for the high acidity, and additional protons that may appear owing to W^{6+} reduction can play only a minor role.

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INTRODUCTION

Heterogeneous acid catalysts have found wide use in practice [1]. Environmental regulations are becoming increasingly stringent, and, hence, hydrocarbon raw materials need deeper processing. Therefore, it is necessary to develop new catalysts [2]. The polyoxide acid catalysts WO_3/MO_2 (M = Zr, Sn, Ti) [3–11] are among the recently discovered and extensively studied catalysts. These catalysts possess a variety of useful properties: high acidity [7, 10], applicability to liquid-phase and gas-phase catalytic reactions, insensitivity to impurities in raw materials, and ease of regeneration (they are thermally stable at least up to 800°C [4]). It is due to the combination of these properties that these materials are interesting to researchers. Although a considerable number of publications have been devoted to these catalysts (primarily WO_3/ZrO_2), we have found no systematic or generalizing investigations. It is difficult to compare catalytic properties, because the catalysts have been synthesized by different authors under a wide variety of conditions (temperature, reactant composition, the order in which the reactants are mixed, etc.) and have been used in various reactions.

Here, we report the preparation of a series of WO_3/MO_2 (M = Zr, Sn, Ti) catalysts, a study of their acid properties by IR spectroscopy and the thermal desorption of pyridine, and our conclusion as to the nature of their acidity. Catalytic activities are compared for liquid-phase cumene hydroperoxide decomposition, a reaction that is easy to carry out and is commercially used in the manufacture of phenol and acetone [12].

EXPERIMENTAL

Synthesis of Catalysts

$ZrOCl_2 \cdot 8H_2O$, a 3 M solution of Ti^{4+} in HCl, $SnCl_2 \cdot 2H_2O$, $SnSO_4$, $(NH_4)_{10}H_2W_{12}O_{42}$ (Na/W = 0.0005 mol/mol), $H_3PW_{12}O_{40} \cdot 15H_2O$ (PW_{12}), and $H_4SiW_{12}O_{40} \cdot 12H_2O$ (SiW_{12}) (Na/W = 0.002 mol/mol after ethereal extraction from an aqueous solution in the presence of HCl) were of reagent grade. $H_6P_2W_{18}O_{62} \cdot 18H_2O$ (Na/W = 0.005 mol/mol) was prepared by electrodialysis [13]. A 0.15 aqueous solution of peroxometatungstic acid $H_6H_2W_{12}O_{40-x}(O_2)_x$ (Na/W = 0.05 mol/mol) was prepared by the electrodialysis of a solution of Na_2WO_4 in the presence of H_2O_2 as described earlier [13]. $SnCl_2 \cdot 2H_2O$, $SnSO_4$, and $(NH_4)_{10}H_2W_{12}O_{42}$ were dissolved in the presence of H_2O_2.

The catalysts were synthesized by two methods. **Method 1:** A W compound and a second element (Sn,

Table 1. Synthetic conditions for the catalysts

No.	Catalyst	Synthetic method	W compound	Temperature, °C	Calcination time, h	S_{BET}, m^2/g
1	30% WO_3/SnO_2	1	$H_6H_2W_{12}O_{40-x}(O_2)_x$	800	6	70
2	30% WO_3/SnO_2	1	$H_6P_2W_{18}O_{62}$	800	6	92
3	30% WO_3/SnO_2	1	PW_{12}	800	6	55
4	30% WO_3/SnO_2	1	$(NH_4)_{10}H_2W_{12}O_{42}$	800	6	46
5	30% WO_3/SnO_2	1	SiW_{12}	800	6	43
6	30% WO_3/SnO_2	1	SiW_{12}	800	6	89
7	40% WO_3/SnO_2	1	SiW_{12}	800	6	24
8	20% WO_3/SnO_2	1	SiW_{12}	800	6	93
9	10% WO_3/SnO_2	1	SiW_{12}	800	6	62
10	5% WO_3/SnO_2	1	SiW_{12}	800	6	42
11	30% WO_3/SnO_2	1	SiW_{12}	600	6	145
12	30% WO_3/SnO_2	1	SiW_{12}	700	6	135
13	30% WO_3/SnO_2	1	SiW_{12}	900	6	54
14	30% WO_3/SnO_2	1	SiW_{12}	800	2	92
15	30% WO_3/SnO_2	1	SiW_{12}	800	4	90
16	30% WO_3/SnO_2	1	SiW_{12}	800	8	76
17	30% WO_3/SnO_2	2	SiW_{12}	800	6	93
18	30% WO_3/ZrO_2	1	SiW_{12}	800	6	33
19	30% WO_3/ZrO_2	2	SiW_{12}	800	6	44
20	30% WO_3/ZrO_2	1	$H_6H_2W_{12}O_{40-x}(O_2)_x$	800	6	26
21	20% WO_3/ZrO_2	1	SiW_{12}	800	6	58
22	20% WO_3/ZrO_2	2	SiW_{12}	800	6	44
23	10% WO_3/ZrO_2	1	SiW_{12}	800	6	22
24	10% WO_3/ZrO_2	2	SiW_{12}	800	6	45
25	30% WO_3/TiO_2	1	SiW_{12}	800	6	13
26	30% WO_3/TiO_2	2	SiW_{12}	800	6	32
27	20% WO_3/TiO_2	1	SiW_{12}	800	6	17
28	20% WO_3/TiO_2	2	SiW_{12}	800	6	42
29	10% WO_3/TiO_2	1	SiW_{12}	800	6	19
30	10% WO_3/TiO_2	2	SiW_{12}	800	6	45

Note: The sources of M are $ZrOCl_2$, a solution of Ti in HCl, and $SnCl_2$ ($SnSO_4$ for sample no. 5).

Zr, or Ti) were mixed in an aqueous solution in an appropriate ratio, their total concentration being 20–40 wt %. The mixture was evaporated to dryness, and the residue was calcined (the conditions are given in Table 1). **Method 2:** An aqueous ammonia solution was introduced into a solution of the mixture obtained by method 1 until pH 9–9.5. The resulting paste was dried at 150°C, and the residue was calcined at 800°C for 6 h.

Catalytic Reaction

Commercial cumene hydroperoxide (CHP, 93.1%, Na content 0.0115 g/l or 5×10^{-4} mol/l) produced at the

Table 2. Composition of aqueous extracts from the catalysts (100°C)

No.	Catalyst	W : M, mol/mol		Amount of washed-off substance, wt %
		in the catalyst	in the extract	
7	40% WO_3/SnO_2	0.55	12.7	2.6
6	30% WO_3/SnO_2	0.28	14	3.4
8	20% WO_3/SnO_2	0.21	8	4.7
9	10% WO_3/SnO_2	0.092	3.7	1.2
10	5% WO_3/SnO_2	0.043	2	1.1
18	30% WO_3/ZrO_2	0.23	5.0	1.4
21	20% WO_3/ZrO_2	0.13	3.7	1.0
23	10% WO_3/ZrO_2	0.059	1.1	0.4
25	30% WO_3/TiO_2	0.15	4.3	0.7
27	20% WO_3/TiO_2	0.086	3.0	1.0
29	10% WO_3/TiO_2	0.038	4.6	1.0
	WO_3	–	–	0

Omsk Plant of Synthetic Rubber (Omsk, Russia) was used. The decomposition of CHP to phenol and acetone was conducted at 40°C for 30 min in a glass reactor with magnetic stirring with a velocity of ~800 rpm. The initial concentration of CHP in cumene and acetone was 0.5 mol/l, the solution volume was 10 ml, and the amount of dry milled catalyst was 0.1 g (for cumene) or 0.04 g (for acetone). CHP conversion was determined iodometrically [12] immediately after stirring was stopped.

Physicochemical Studies

Aqueous extracts were obtained by keeping a sample (1 g) in water (20 ml) at 100°C for 30 min followed by centrifugation. Chemical analyses were carried out by atomic absorption spectrometry with plasma ionization.

In acidity studies, a dry (300°C) sample (1.5 g) was stirred at room temperature with a 0.24 M solution of pyridine (15 ml) in benzene and was dried at 100°C for 1 h *in vacuo*. The thermal desorption of pyridine was studied by DTA–TG on a Q-1500D MOM thermal analyzer at a heating rate of 10 deg/min in air using 0.5-g samples. The accuracy of weight determination was 0.2 mg.

In order to determine the acidity on the proton affinity (*PA*) scale, catalyst powders were compacted into thin pellets (30–40 mg/cm^2). Before pyridine adsorption, the pellets were pumped at 250°C. Next, a portion of pyridine nearly equivalent to the number of strong acid sites in the catalyst was injected into the adsorption chamber at 150°C. IR spectra were recorded at room temperature on a Shimadzu FTIR-8300 spectrophotometer with a resolution of 4 cm^{-1} with averaging of 100 accumulated spectra. The strength of protonic sites was characterized as described earlier [14] by a *PA* value calculated using the equation $PA = [\log(3400 - \nu_{NH})]/0.0023 - 51$, where *PA* is the energy of proton abstraction in kJ/mol, 3400 cm^{-1} is the position of the band of the unperturbed N–H bond for the pyridinium ion, and ν_{NH} is the center of gravity of the stretching band of the pyridinium ion determined from the contour of the line at 3400–1800 cm^{-1}.

Electronic micrographs of the catalyst surface were obtained on a BS-350 Tesla scanning electron microscope. IR spectra were recorded as KBr pellets on a Shimadzu FTIR-8300 spectrophotometer at 400–1800 cm^{-1}.

RESULTS AND DISCUSSION

The data in Table 1 allow general conclusions to be drawn as to the influence of synthetic conditions and of the composition of catalysts on their surface area. The surface area decreases with an increase in the calcination temperature and time. SnO_2 should be preferred to ZrO_2 or TiO_2, and method 2 (coprecipitation) gives better results than synthesis from homogeneous solutions. The influence of traces of other elements (P, Si) is ambiguous. Apparently, they cause no dramatic changes.

Study of Aqueous Extracts of the Catalysts

Although the catalyst components (oxides) taken separately are water-insoluble, the catalysts can partially be dissolved in water [7, 15], indicating that new structures differing from the binary oxides or their solutions form during high-temperature synthesis. We attempted to study this phenomenon in greater detail.

The 30% WO_3/SnO_2 sample (no. 1, 3 g) was stirred in water (11 ml, pH$_0$ 5.5) at 22°C. The pH value of the aqueous suspension was measured to be 2.8 in 5 min, 2.3 in 15 min, 2.0 in 30 min, and 1.8 in 1 and 2 h. Then the catalyst was dried for 1 h at 150°C and washed again, resulting in pH 3.5 in the aqueous extract. The catalyst was dried at 150°C, and pH 5.5 was measured in the third aqueous extract. However, the aqueous extracts from the catalyst calcined at ≥600°C were acidic again. The total amount of matter washed out at 22°C was 1.5 wt % (5–10 times greater than is lost in a catalytic run). According to chemical analysis, the substance washed out is enriched in tungsten: W/Sn = 1.2 mol/mol against W/Sn = 0.28 in the original sample. We failed to isolate the pure washed-off substance: during slow evaporation at room temperature, the substance gradually decomposes to a yellowish insoluble precipitate (heating accelerates the decomposition reaction). The IR spectrum of this precipitate is identical to that of H_2WO_4 (a broad absorption band at 500–900 cm^{-1}). The only exceptions are catalyst nos. 2 and 3: their extracts contained the heteropolyacid PW_{12}, although most of the phosphorus remained in the catalyst, as was indicated by IR data.

The water-soluble phase is present in all of the catalysts studied (see Table 2), and its amount depends insignificantly and ambiguously on the sample composition. Remarkably, in all cases, the washed-off phase is considerably enriched in tungsten. This suggests that the catalysts contain polytungstic compounds that are weakly bound to the supporting oxide and can be washed off with water, an organic reaction medium [7, 15], or aqueous ammonia [16]. These compounds can only be polyoxometalates (POMs; in protonic form, they are iso- or heteropolyacids), which consist of ensembles of WO_6 octahedra and can contain other ions, including M^{4+} [17, 18]. This conclusion agrees with the current views of catalyst structure [10, 15, 19].

POMs were precipitated from aqueous extracts by the addition of tetrabutylammonium bromide (POM salts with tetrabutyl ammonium are completely insoluble in water) and were purified by dissolution in acetonitrile, filtration for MO_2 removal, and precipitation with water. The IR spectra of all the salts, regardless of the initial catalyst composition (except for nos. 2 and 3), are quite the same and are identical to the spectrum of the metatungstate ion $H_2W_{12}O_{40}^{6-}$ [20], which is stable in acidic aqueous solutions. Since metatungstic acid itself is thermally very unstable [18], it is unlikely that it is formed during high-temperature synthesis. Evidently, the washed-off POM is formed during the solid-phase synthesis and then decomposes to a stable POM and $MO_2 \cdot xH_2O$. Note that the known heteropolyacids are stable only below 500°C [18] and the high-temperature POM synthesis involving MO_2 is a new, obscure phenomenon.

IR Spectra of the Catalysts

The IR spectra of the catalysts (Fig. 1) show a broad absorption band at 400–1000 cm^{-1} from MO_2 on which weak bands at 800–820, 860–880, and 960–1000 cm^{-1} are superimposed. The latter are characteristic of the W–O–W and W=O bands and are usual for the spectra of POMs[20]. In our opinion (and according to other researchers [10, 15, 19, 21]), these bands are strong evidence of the existence of POM in the WO_3/MO_2 samples calcined at 600°C and above. Their intensity is maximum for M = Sn (the intensity depends slightly on synthesis conditions, but P and Si inclusions exert a negative effect) and is lower for M = Zr. For M = Ti, these bands are not observed at all. The IR spectra of the samples washed-off with water remain almost unchanged. In other words, the catalysts contain a weakly bound (extractable) POM and high proportions of strongly bound, polytungstic, POM-like structures.

Electron Microscopic Examination of a Catalyst

According to SEM data (Fig. 2a), the 30% WO_3/SnO_2 catalyst (no. 1) consists of faceted particles with sizes up to several hundreds of micrometers. In

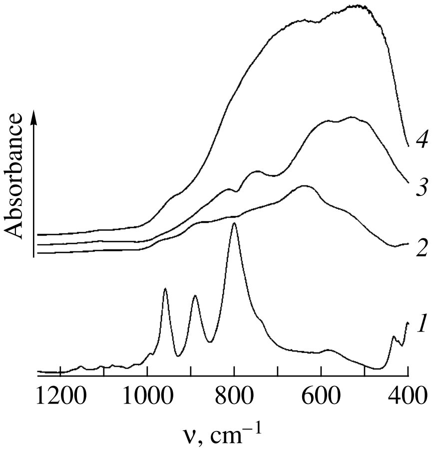

Fig. 1. IR spectra: (*1*) tetrabutylammonium POM salt from the aqueous washings of a catalyst, (*2*) 30% WO_3/ZrO_2 (no. 19), (*3*) 30% WO_3/SnO_2 (no. 6), and (*4*) 20% WO_3/TiO_2 (no. 28).

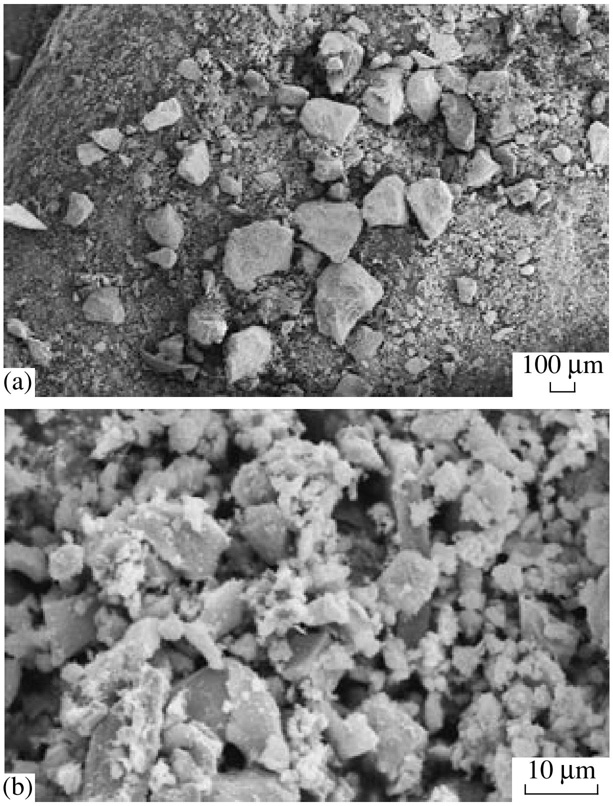

Fig. 2. Electron micrographs of the 30% WO_3/SnO_2 catalyst (no. 1): (a) catalyst granules and (b) surface of a large particle.

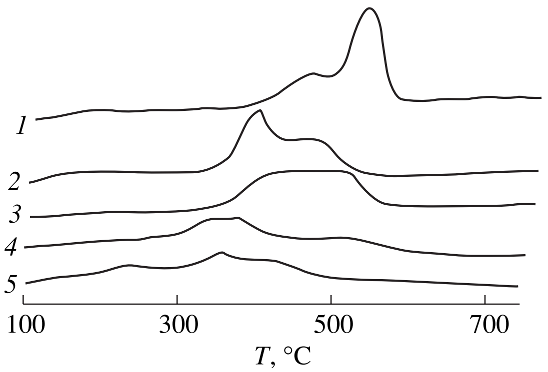

Fig. 3. DTA curves for pyridine desorption from (*1*) PW_{12}, (*2*) 30% WO_3/SnO_2 (no. 6), (*3*) 30% WO_3/SnO_2 (no. 14), (*4*) 30% WO_3/ZrO_2 (no. 19), and (*5*) 30% WO_3/TiO_2 (no. 26).

view of our earlier data [7], these particles can be assigned to the SnO_2 phase (the crystalline phase WO_3 is absent). The surface of these particles (Fig. 2b) is covered by chaotic conglomerations of fine (SnO_2?) crystals, shapeless particles (probably containing strongly bound W, which is undetectable by X-rays), and some "mustiness." The latter, as judged from its relatively small amount and openwork structure, is the extractable POM phase.

Acidity of the Catalysts

The acidity of the 30% WO_3/SnO_2 (no. 1), 30% WO_3/ZrO_2 (no. 20), and 30% WO_3/TiO_2 (no. 25) catalysts on the *PA* scale is 1140 ± 20 kJ/mol, which is equivalent to the strength of the strong heteropolyacids $H_4SiW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ [14].

After pyridine adsorption, the IR spectra of the samples, except for 5% WO_3/SnO_2 (no. 10), contain absorption bands at 1535 and 1488 cm^{-1} corresponding to pyridine molecules protonated at Brønsted acid sites. These bands are typical of these kinds of catalysts [19, 22, 23], as well as heteropolyacids [14], which are representative protonic acids [18]. The intensity of these bands varies in the same way as the intensity of the absorption bands at 800–1000 cm^{-1} and the number of acid sites (Table 3). The intensity is the highest for the 30% WO_3/SnO_2 catalysts. At the same time, their spectra contain no absorption band at 1450 cm^{-1} due to pyridine molecules adsorbed on Lewis sites. This band is observed [19, 22, 23] for catalysts with a low WO_3 content (6–15% in different publications).

The acidity was quantitatively studied in detail by the DTA–TG method for samples containing preadsorbed amine. Although NH_3 is most frequently used as amine, we employed pyridine, which is more appropriate for studying the surface protonic acidity [24–26]. We determined the amounts of weak, medium, and strong acid sites (which desorb Py at 100–200, 200–300, and >300°C, respectively); the plateau temperature of the TG curve (complete Py removal); and the peak positions in the DTA curve. Data for two heteropolyacids and the SO_4/ZrO_2 catalyst (3% S) are given for comparison (Table 3).

In the DTA curves (Fig. 3), an endotherm below 300°C due to Py desorption (not shown in Fig. 3) was observed only for some catalysts. Therefore, weak and medium acid sites are absent in most of the samples. To the contrary, pronounced exotherms were observed for all samples in the range from 250 to 600°C. It follows from these data that Py molecules adsorbed on strong acid sites are oxidized with oxygen more rapidly than they are desorbed. Therefore, the positions of the exothermic DTA peaks and the flattening-out temperatures of the TG curves cannot be directly correlated with the strength of the acid sites on the catalyst surface. Probably, the thermoanalytical curves (Fig. 3) result from the interplay of differently acting factors, including acid–base interactions, oxidative catalysis by the surface of the polyoxide material, and the catalyst texture. A similar conclusion was made after the detailed study of the thermal desorption of Py from SO_4/ZrO_2 catalysts [27]. However, it is obvious that if a Py molecule undergoes thermal destruction only at 450–500°C (regardless of whether it does so while adsorbed or immediately after desorption), this molecule is from a strong acidic site on the surface. Thus, it follows from the data in Table 3 and Fig. 3 that the most acidic materials are the heteropolyacid PW_{12} (whose exothermic peak at 560°C is due to the decomposition of the POM anion, like the exothermic peaks at 510 and 530°C for SiW_{12} [28], and is possibly overlapped with the Py desorption peak) and WO_3/ZrO_2, whereas WO_3/SnO_2 and WO_3/TiO_2 contain active sites with a wider variety of properties.

With the accepted classification of acid sites into weak, medium, and strong, the TG data (Table 3) quite adequately reflect the strength distribution of the sites. Some deviations can be observed only for WO_3/TiO_2, whose DTA curves exhibit low-intensity exothermic peaks below 300°C. Heteropolyacids, which are strong protonic acids [14, 18], possess exclusively strong acid sites. WO_3/MO_2 contains sites of various strengths, strong acid sites prevailing (except for sample nos. 7, 10, and 21). The total number of sites (per gram) is the largest for M = Sn. Varying the WO_3 content (sample nos. 6–10) has demonstrated that 40% WO_3/SnO_2 and 5% WO_3/SnO_2 have the lowest acidity (due to a decrease in the amount of strong sites). The overall acidity decreases with an increase in the calcination temperature (nos. 6, 11–13), and the calcination time at 800°C is not a crucial factor. As for the starting reactants, $SnCl_2$ is preferred to $SnSO_4$, and $H_6P_2W_{18}O_{62}$ and $H_6H_2W_{12}O_{40-x}(O_2)_x$ are better than the other WO_3 sources. In all cases, especially for M = Zr and Ti, synthesis method 2 gives better results than method 1.

Table 3. Acidity of the catalysts determined by pyridine thermal desorption and their catalytic activity

No.	DTA peak positions, °C	TG plateau temperature, °C	Acid site content, μmol/g				CHP conversion, %	
			weak	medium	strong	total	in cumene	in acetone
WO_3/SnO_2								
1	450, 605	520	72	47	206	325	40	94
2	420–500	530	101	139	341	581	36	95
3	430, 500	520	56	33	139	228	8	11
4	400–565	530	51	57	132	240	40	91
5	415–535	530	47	35	82	164	5	13
6	415, 475	510	68	45	127	240	30	63
7	450	500	63	50	51	164	3	0
8	450, 615	530	82	89	202	373	37	57
9	450–610	530	82	52	163	297	24	33
10	445	500	82	48	84	214	3	0
11	550	520	108	126	344	578	6	8
12	425	520	70	90	270	430	28	55
13	390, 495	530	61	45	96	202	44	97
14	450–550	530	40	63	175	278	30	82
15	450–550	530	63	63	164	290	38	90
16	340, 415, 500	530	38	66	149	253	44	88
17	430, 520	530	25	50	190	265	42	78
WO_3/ZrO_2								
18	350, 500	530	38	28	55	121	40	10
19	345, 380, 515	530	35	29	58	122	32	6
20	380, 515	520	35	35	60	130	32	10
21	320, 375	510	33	25	28	76	23	1
22	415	530	46	71	78	195	44	91
23	355	510	20	10	26	56	16	1
24	385	520	25	25	50	100	25	9
WO_3/TiO_2								
25	350, 445	490	32	19	50	101	51	2
26	260, 380, 450	510	68	46	101	215	13	2
27	260, 380, 445	505	0	15	40	56	97	21
28	270, 405, 455	490	25	28	73	126	27	20
29	245, 365, 440	500	19	19	50	88	80	9
30	265, 390, 455	500	25	25	64	114	97	68
PW_{12}	475, 560	580	0	0	1010	1010	–	–
SiW_{12}	420, 510, 530	540	0	60	1390	1450	–	–
SO_4/ZrO_2*	–	550	–	–	–	96	–	–
WO_3	–	–	–	–	–	–	0	0

* From the DTA curve of pyridine [26].

Catalytic Properties

The following catalysts are the most active in CHP decomposition, providing a CHP conversion of >90% (Table 3): 30% WO_3/SnO_2 (sample nos. 1, 2, 4, 13), 20% WO_3/ZrO_2 (no. 22) (in acetone), 20% WO_3/TiO_2 (no. 27), and 10% WO_3/TiO_2 (no. 30) (in cumene). The activity of the catalysts is not related to their overall acidity, in agreement with the absence of such correlations for solid catalysts [25–29], including WO_3/ZrO_2 [30], and even for soluble heteropolyacids [31]. The strong solvent effect was also quite predictable [32–34]. The nature of the solvent often has an effect on the reaction mechanism [34], including that the mechanism of CHP decomposition is under the action of acids [35]. Effective acidity depends not only on the chemical properties of the Brønsted acid sites but also on the structure of the catalyst itself and on the environment of the sites [36]. For WO_3/MO_2, the notion of the active site structure is presently speculative and the active phase compositions and their dependence of M and synthesis conditions are unknown. Note only that, for M = Sn, the 30% WO_3/SnO_2 catalysts calcined for 6 h at 800–900°C are the most active, as in the case of some other reactions [7]. Among the less carefully examined catalysts with M = Zr or Ti catalysts with a lower WO_3 content are more active.

It is important to determine the contribution from the different phases constituting the catalysts to the catalysis of the liquid-phase reaction. For this purpose, some catalysts were washed with water to remove the soluble phase, dried at 150°C for 1 h, and tested in the reaction. This treatment reduces their activity to various extents (Table 4). However, if the catalysts are calcined again at 600°C after water treatment, then their activity is fully restored (except for sample no. 2). In another experiment with catalyst no. 1, after stirring was stopped, the reaction mixture was separated from the solid phase by centrifugation, a fresh portion of CHP was added to the solution, and the reaction was resumed. The CHP conversion was 53%. Thus, most of the WO_3/MO_2 catalyst and its extractable component are active in the acid-catalyzed reaction. The contribution from the latter to catalysis is very large considering its low weight content (Table 2). Evidently, this phase is the most acidic component (POM) of the catalysts. It is due to its higher percentage in the WO_3/SnO_2 catalysts that these catalysts are more acidic and show a higher activity in the catalytic reactions. Therefore, optimizing the synthesis conditions in order to maximize the POM content is a very important, but not the only, way of enhancing the efficiency of the WO_3/MO_2 catalysts.

Table 4. Data characterizing CHP decomposition in acetone in the presence of water-treated catalysts

No.	Catalyst	CHP conversion, %		
		starting catalyst	catalyst washed-off with water	catalyst regenerated for 1 h at 600°C
1	30% WO_3/SnO_2	94	84	91
2	30% WO_3/SnO_2	95	73	62
4	30% WO_3/SnO_2	91	59	91
15	30% WO_3/SnO_2	90	45	90
22	20% WO_3/ZrO_2	91	86	93

Nature of Active Sites in the Catalysts

Two viewpoints as to the nature of the Brønsted acidity of WO_3/MO_2 catalysts prevail among the researchers: (1) W is organized like a POM, whose protonated forms are very strong acids [7, 10, 15, 19]; (2) proton sites appear during the catalytic reaction due to the partial reduction of W^{6+} [6, 37–39]. There is also a compromise opinion [10]. When the reaction occurs in an oxidative medium (e.g., benzene nitration [9] and CHP decomposition), W^{6+} cannot be reduced. Nevertheless, the catalysts exhibit a high activity. Therefore, they gain a high acidity during the synthesis, and extra protons forming in the reductive medium (such as in hydrocarbon isomerization) only contribute to the overall acidity.

Although, according to spectroscopic data, the WO_3/MO_2 catalysts manifest only Brønsted acidity (at least the samples with a WO_3 content of 20 wt % and above), sometimes (e.g., in sorbose acetonation [7]) they exhibit anomalous catalytic properties that are not typical of protonic acids. Perhaps (and even very probably), the texture and structure of the material and the environment of acid sites play an important role in catalysis by WO_3/MO_2 and MoO_3/MO_2.

Thus, the WO_3/MO_2 catalysts (with M = Sn, Zr, Ti, and probably Hf) are strong Brønsted acids of one type. They contain at least two phases active in acidic catalysis, of which at least one phase is POM (heteropolyacid). These phases form during high-temperature synthesis and are responsible for the high acidity of the materials. Extra protons that possibly appear owing to W^{6+} reduction can play only a minor role.

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