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Influence of the coordination on the catalytic properties of supported W catalysts

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Abstract

Zirconia supported W catalysts were prepared using anionic exchange from a peroxo-tungstate solution and zirconium hydroxides of high surface areas. These solids contain about 20 wt% W, and retain a surface area of about 120 m^2/g after calcinations in air at 873 K, temperature at which their acidity is maximum. Raman spectroscopy shows the presence of tetrahedral W at low temperature, sintered to polytungstates by calcination at 873 K and WO_3 at 973 K. These catalysts are active for the oxidation of dibenzothiophene by hydrogen peroxide. The solids containing tetrahedral W cations show higher activity than clusters of WO_3. The reaction can be performed with good oxygen selectivity with H_2O_2 in 2-butanol as solvent, or in decane with *tert*-butylhydroperoxide as oxidizing agent. The catalysts can be recycled without loss of performances.

Keywords: Peroxotungsten; Anionic exchange; Zirconia; Coordination of W; Acidity; Oxidation of dibenzothiophene; Sulfone

1. Introduction

Transition metals ions supported on an inert matrix offer, like in the case of solid solutions [1], a mean of investigating the influence of the symmetry of the catalytic site on the reactivity. This approach was applied successfully to evidence the effect of surface structure of Mo oxides on the allylic oxidation of olefins [2]. The results were later substantiated by the study of oriented oxides [3,4]. Similar results were obtained with oriented W oxides [5] showing an effect of coordination in that case also. It is, however, difficult to obtain supported model catalysts in which the coordination of W is controlled. An example of these catalysts is W/ZrO_2 which have been thoroughly investigated, with the conclusion that their catalytic properties change significantly with the preparation [6]. Both impregnation with aqueous ammonium metatungstate [7,8] and coprecipitation using sol–gel [9,10] have been proposed. It is reported that high acidity requires both tungsten loadings in excess of monolayer coverage and calcination in air above 1073 K. Raman studies suggest that W is then in octahedral coordination mainly as WO_3 clusters [11–13] or polyoxotungstate clusters [14]. Near-edge X-ray absorption spectra of dehydrated WO_x–ZrO_2 within a wide range of WO_x surface density (3–15 $W\,nm^{-2}$) also showed that W^{6+} centers are present in distorted octahedral coordination ascribed to polytungstates and crystalline WO_3 which coexist at the zirconia surface [15].

Another approach is to use anion exchange on basic supports. Since the chemistry of W is very pH sensitive many different species can be obtained, among them tetrahedral W^{6+} at pH > 7. This coordination could be obtained by exchange of ${WO_4}^{2-}$ onto the surface. This preparation has been reported with hydrotalcites, using metatungstate at pH 9, conditions at which ${WO_4}^{2-}$ is formed [16–18]. An acid medium is more favorable for anionic exchange with a weak base as ZrO_2. Indeed mononuclear peroxotungstates $W(O_2)_n(O_{4-n})^{2-}$ are formed by dissolution of WO_3 in H_2O_2 [19], yielding an acidic solution which can be used for the exchange of tungsten at the surface of solid bases. We illustrate here the potentialities of this technique to synthesize tungstated zirconia.

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W is well known to be one of the most active oxidation catalyst with H_2O_2 [20]. The catalytic properties have been related to the Lewis acidity of the W oxides, which is thought to change with its coordination. The same W compounds also catalyze the oxidation of sulfides to sulfoxides and sulfones which are important as commodity chemicals and, in some cases, as pharmaceuticals. The homogeneous oxidation of aryl and alkyl sulfides by dilute hydrogen peroxide has recently been reviewed by Sato et al. [21] who used as catalyst a mixture of sodium tungstate and phenylphosphonic acid, with methyltrioctylammonium hydrogensulfate as phase-transfer agent. According to the authors this catalyst is the first efficient active system promoting the reaction under organic solvent- and halogen-free biphasic conditions. Indeed these reactions are very sensitive to solvent effect, and the authors point out that most earlier procedures require either chlorohydrocarbon solvents that affect human health and environment, or anhydrous H_2O_2, which has to be handled with great care.

The liquid oxidation of sulfides has also been investigated in the context of oxidative desulfurization of diesel oils [22]. It is well known that sterically hindered alkyldibenzothiophenes, due to their low reactivity, are difficult to desulfurize on conventional HDS catalysts. Using high temperatures would cause yield loss, faster catalyst coking, and product quality deterioration (e.g., color). Using high pressure requires a large capital outlay, and it has then been attempted to convert sulfides into compounds easier to separate. Gore [23] used peracids which do not require catalysts, and Ho et al. used H_2O_2 or hydroperoxides activated by $(HMPT)MoO(O_2)\cdot 2H_2O$ [24]. Gore et al. [25] later performed thiophene oxidation with hydrogen peroxide and acetic acid as extraction solvent, achieving both HDS and HDN in the same process.

Only a few examples of heterogeneous oxidation of sulfides have been published. Hulea and Moreau reported the oxidation of ethylsulfide to the sulfoxide by H_2O_2 using TS1 and Ti-Beta [26]. This oxidation of thioethers with H_2O_2 or *tert*-butylhydroperoxide (TBHP) yielding sulfoxides has been reported by Fraile [27] on Ti/SiO_2, while Rabion et al. [28,29] reported the use of Fe-phtalocyanines as homogeneous catalyst and TS1 or Ti-BEA as heterogeneous catalysts for the oxidation of thiophene derivatives to sulfones. These reactions on titanosilicates are very sensitive to solvent effects, and the best solvents are CH_2Cl_2 in the case of TBHP, and pure acetonitrile or methanol for the titanosilicates, and a mixture acetonitrile/water (pH 7.7) to solubilize the phtalocyanine in that of H_2O_2. These solvents are not quite satisfactory for industrial use since they are considered as toxic or dangerous for environment. The choice of a solvent is related to the type of catalyst and oxidation agent, therefore the proposal of other solutions requires another type of catalyst. We investigate here the preparation of tetrahedral W^{6+} cations supported on zirconia and their catalytic properties for the oxidation of dibenzothiophene (DBT) in different solvents.

2. Experimental

2.1. Materials

Two supports were used: a commercial Zr hydroxide from MEL Chemicals (surface area 309 m^2/g) and a home made zirconia. This hydrated zirconium hydroxide was precipitated at pH 9 from a 0.4 M solution of $ZrOCl_2$, $8H_2O$ (100 ml), and an ammonia solution (28%). The resulting suspension was aged for 2 h, separated by centrifugation, and washed with deionized water until complete elimination of chloride anions in the filtrate. The white gel was dried at 383 K for 22 h and crushed in an automatic equipment. The as-synthesized zirconium hydroxide will be abbreviated Zr(OH).

A preparation (ZW_I) was done following the method described in the literature by Barton et al. [30], based on incipient wetness impregnation using ammonium metatungstate as precursor. One gram of Zr(OH) was impregnated, at ambient temperature, by 0.29 ml of a metatungstate aqueous solution (0.23 M) and stirred for 1 h. The resulting solid was dried at 383 K for 12 h and then calcined at 1073 K for 3 h under a dry air flow (20 $cc\,min^{-1}$).

The anionic exchange between the H_2WO_5 solution obtained by dissolving WO_3 (Aldrich) in H_2O_2 (Prolabo) and zirconium hydroxide was done by adding 10 g of zirconium hydroxide to 150 ml of a H_2WO_5 solution under stirring. Different H_2WO_5 concentrations were used: 0.01, 0.1, 0.25, and 0.5 M. The suspension was kept under stirring for 15 min, and then the solid was filtered, washed with distilled water, and dried at 353 K for 24 h, and then eventually calcined at different temperatures.

2.2. Characterizations

Chemical analyses were performed by ICP after dissolution of the sample. XRD patterns were obtained on a Bruker D5005 instrument, using Cu-Kα radiation. BET surface areas were determined from the isotherms of N_2 adsorption at 77 K measured with an automated volumeter on solids desorbed in situ at 523 K in vacuum. Raman analysis was performed on a DILOR XY spectrometer using the 514.53 nm line of an Ar–Kr laser. The power on samples was 10 mW and spectral resolution typically of 3.1 cm^{-1}. The spectra were usually recorded at room temperature. A spectrum was recorded at 473 K after calcination at 973 K using a TS1500 Linkam Cell.

Acidity measurements were performed by gravimetry using a Setaram DTA-DTG apparatus coupled with a mass spectrometer. The total amount of acid sites was drawn directly from the amount of ammonia irreversibly adsorbed at 373 K. The samples were first evacuated in situ at 673 K for 2 h under flowing He, then He was replaced by a mixture containing 0.5% NH_3 in He, and the weight was recorded. When the steady state was reached, the weakly bonded ammonia was removed flushing with pure He at the same temperature.

Pyridine adsorption was measured by infrared spectroscopy on a Vector 22 Brucker spectrometer using self-supported wafers. Pyridine was adsorbed under saturated vapor pressure, at ambient temperature, on the samples previously evacuated at 673 K. Then, the samples were desorbed for 1 h at ambient temperature, 423, 473, 573, and 673 K.

2.3. Catalytic measurements

The oxidation of dibenzothiophene by hydrogen peroxide was studied in a batch reactor composed of a triple necked 50-ml round-bottomed flask, which was heated to 333 K in an oil bath. In a typical experiment 0.5 mmol of DBT (Aldrich), 10 ml of acetonitrile as the solvent, and 0.51 ml of hydrogen peroxide were introduced. The reactor was swept with a flow of nitrogen to remove CO_2 from the atmosphere and stirred at 450 rpm. When thermal equilibrium was reached, the catalyst (0.1 g), dried at 373 K, was introduced; the progress of the reaction was followed by gas chromatography using a DB5 column. An external standard was used for the chromatographic analysis: an aliquot of the reaction medium was taken and diluted in methanol containing a fixed amount of hexanol. DBT was converted exclusively into sulfone, with a carbon balance better than 95%. The degree of advance of the reaction was measured using the conversion of DBT. Part of the H_2O_2 reagent was decomposed into oxygen, determined by volumetric measurement:

$$H_2O_2 \rightarrow H_2O + 1/2O_2.$$

The material balance of oxygen was established by considering the amount of oxygen converted to sulfone and the amount of gas evolved during the reaction. From this experimental measurement, the selectivity $S_{(O2)}$ of decomposition of H_2O_2 into oxygen is expressed as a ratio: the number of moles of oxygen evolved/half the number of moles of H_2O_2 engaged in the reaction.

3. Results and discussion

3.1. Preparation of the catalyst

The solution of peroxotungstate in H_2O_2 is acidic and reaches a pH < 1, favorable for anion exchange. As illustrated in Table 1, for exchange solutions in the range 0.1–0.5 M, the chemical composition of the solids made with the homemade zirconia is independent of the concentration, and reaches $\approx 20\%$ showing saturation of the exchange sites. The same composition is achieved when exchanging the MEL support with a 0.12 M solution. Samples of lower W content were prepared using solutions of lower concentration, containing the desired amount of W.

Table 1
Chemical composition of the W/ZrO_2 samples

Concentration of the solution	wt% W in the solid
0.01	3
0.1	19.4
0.12	20.6
0.25	19.6
0.5	20.8

Table 2
Surface areas of the samples prepared from MEL zirconia after evacuation at 573 K

Sample	wt% W	$S_{\text{tot BET}}$ (m^2/g)	$V_{\text{micropores}}$ (ml/g)
Support	0	308.8	0.085
Zr-2	2.1	313.6	0.083
Zr-3	5.2	349.3	0.087
Zr-4	10.2	370.7	0.103
Zr-1	20.6	295.5	0.044

Table 3
Surface areas of samples prepared from homemade zirconia with different W contents, after calcination at 873 or 1073 K

Calcination temperature (K)	Molar H_2WO_4 concentration ($m^2\ g^{-1}$)			ZW_I ($m^2\ g^{-1}$)
	0.1	0.25	0.5	
873	96	121	125	
1073	55	44	43	44

Within experimental error, the surface of W/ZrO_2 is the same as that of the support before calcination, as illustrated in Tables 2 and 3. Earlier results showed that the surface area of pure zirconia decreases from about 300 to 60–80 m^2/g after calcination at 873 K [31]. As expected W stabilizes the surface area against sintering since the residual surface area after calcinations at 873 K reaches 125 m^2/g. The stabilizing effect of WO_4^{2-} anions is similar to that of sulfates and can be related to the substitution of OH by more stable anions.

The original zirconia gel shows an average pore size of 1.4 nm after desorption at 523 K. The pore size of the ZrW catalysts is slightly higher and reaches 1.6–1.8 nm after calcinations at 873 K and is shifted in the range 4–8 nm by calcinations at 1073 K. A mesoporous solid is then obtained. The impregnated sample exhibits a surface area of 44 m^2/g after calcination at 1073 K and pore sizes in the range 4–18 nm.

3.2. XR diffraction

After drying at 373 K, W/ZrO_2 is X-ray amorphous. The powder patterns obtained after calcinations at different temperatures are reported in Figs. 1 and 2. When the W content is lower than the zirconium hydroxide exchange capacity, as in $ZW_{0.01}$, the solid is mainly converted to the monoclinic form, as is well known for pure zirconia. By contrast the samples containing about 20 wt% W content are nanocrystallized after calcination at 873 K. Above 873 K, the tetragonal phase, which is normally an intermediate, grows and is stable here up to 1173 K. The diffraction lines of

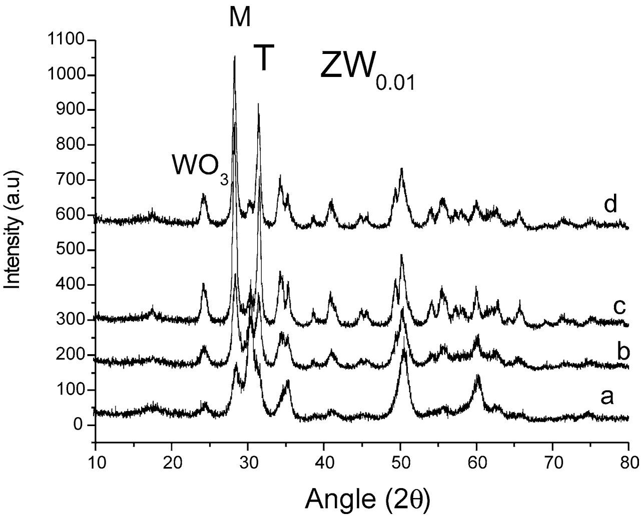

Fig. 1. XRD powder patterns of $ZW_{0.01}$ after calcination at: (a) 873 K, (b) 973 K, (c) 1073 K, and (d) 1173 K.

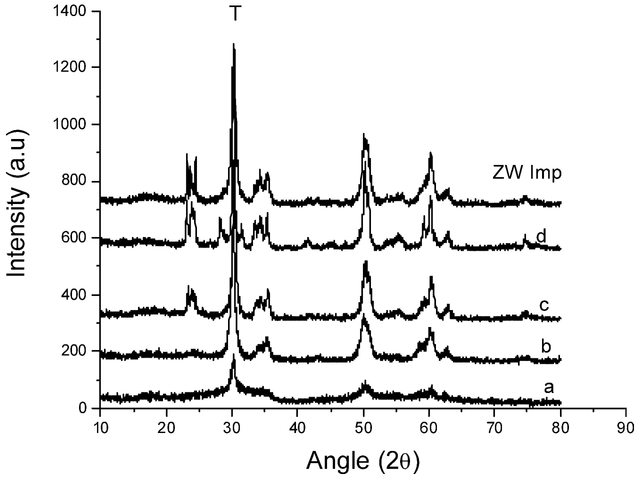

Fig. 2. XRD powder patterns of $ZW_{0.25}$ after calcination at: (a) 873 K, (b) 973 K, (c) 1073 K, (d) 1173 K and ZWI calcined at 1073 K.

WO_3 appear after calcination at 1073 K when the W content is high, and at much lower temperature at low content, suggesting that the solid-state transformation of the support also provokes sintering of WO_3. The sample prepared by incipient wetness impregnation (Fig. 2) shows as expected the lines of tetragonal zirconia and WO_3 as reported earlier by Barton et al. [30]. Srinivasan et al. [32] have proposed that surface sites that adsorb oxygen at low temperatures (298–500 K) are responsible for causing the tetragonal–monoclinic transformation at low temperatures. The incorporation of sulfate covers these sites and inhibits the tetragonal–monoclinic transformation. Tungsten anions plays the same role as sulfates and the effect should be related to the dispersion of W, then the blockage of the transformation up to 1173 K as observed here is in agreement with that hypothesis.

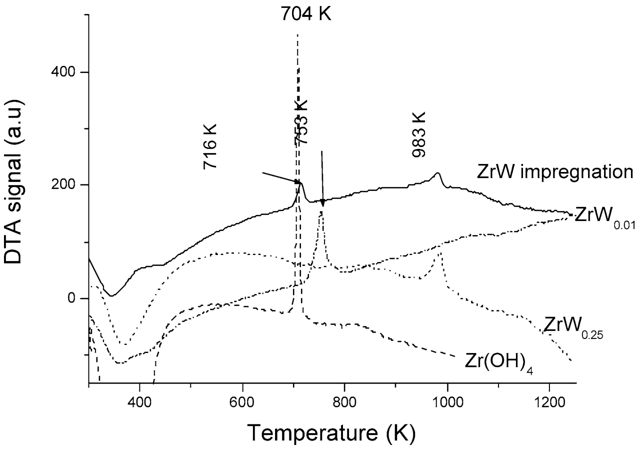

Fig. 3. Thermal analysis of the transformations of pure zirconia and of W/ZrO_2 prepared by impregnation or anion exchange.

3.3. Thermal analysis of the solids

The DTA traces reported in Fig. 3 show the usual crystallization of pure zirconia at 704 K. The TGA curve of the sample prepared by anionic exchange with a 0.25 M W solution shows a high temperature phenomenon at 983 K. This result is comparable to that obtained on zirconium hydroxide exchanged with sulfates. In that case, the glow exotherm characteristic of pure zirconia is suppressed by the presence of sulfates and the phase transition is observed at much higher temperature [33]. Interestingly for the sample prepared by impregnation with equivalent W loading two weak exothermal events occur, at low and high temperature. They suggest that unmodified and WO_x-modified zirconia particles could coexist on the catalyst surface when prepared by impregnation. Finally, the Zr sample exchanged with low WO_x amount shows a single exothermal peak, however, slightly shifted to the higher temperatures as regards to pure zirconia. These set of TGA results suggests that anionic exchange leads to a homogeneous modification of the zirconia crystallization contrarily to the impregnation method.

3.4. Raman analysis

The Raman spectra of $ZW_{0.25}$ containing 20 wt% W and just dried at 373 K have been recorded at room temperature and at 473 K after calcination at 973 K (Fig. 4). At room temperature, the spectrum shows the presence of lines at 940 and 840 cm^{-1} corresponding to the ν_1 symmetric and ν_3 antisymmetric stretching vibrations of tetrahedral W^{6+} cations [34,35]. This spectrum corresponds to an oxotungsten species and it can be concluded that the peroxo species has been decomposed upon drying. The spectrum recorded after cooling down to 473 K, contains the four lines at 1019, 900, 824 cm^{-1} attributed to ν(W=O), ν(W–O–Zr), and ν(W–O–W), respectively [36], and at 645 cm^{-1} due to t-ZrO_2. Additional bands typical of t-Zr–O_2 are observed at 455, 310, and 270 cm^{-1} (not shown). This spectrum is

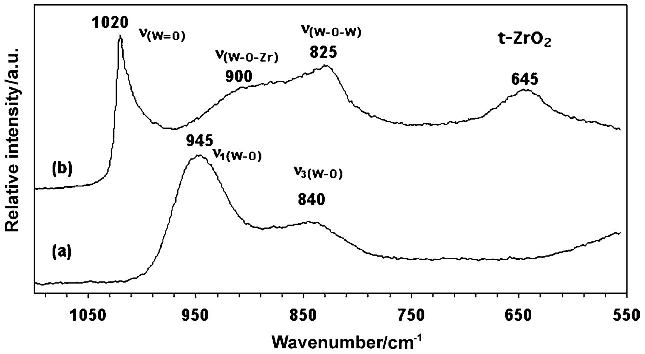

Fig. 4. Raman spectra of $W_{0.25\,M}$ performed (a) after drying at room temperature under ambient air (b) at 473 K after calcination at 973 K.

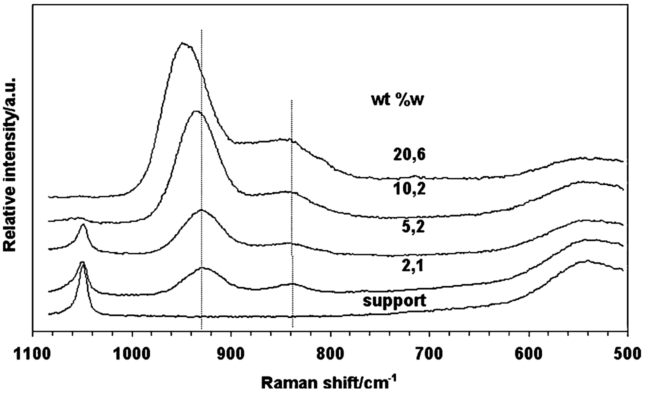

Fig. 5. Raman spectra of W/ZrO_2 samples with various W contents performed at room temperature under ambient air after drying at 373 K.

similar to that reported for a sample prepared by impregnation of $ZrO_x(OH)_{4-2x}$ with aqueous suspensions of ammonium metatungstate followed by drying and calcination at 923 K [14]. The formation of W–O–W bonds proves the formation of polynuclear clusters here also, then the modification of the W environment, from an originally tetrahedral mononuclear species to isopolytungstates by condensation at relatively low temperatures.

The room temperature spectra of catalysts exchanged with various W contents and just dried at 373 K are reported in Fig. 5. They contain the lines attributed to tetrahedral W and a line close to 1050 cm^{-1}, which disappears for a W content of about 10% and has been attributed to carbonates neutralizing the basic sites unoccupied by tungstates at low W content.

Tetrahedral W species have been reported earlier at low concentrations [34], but disappeared at higher concentrations due to condensation. The interesting point is that the preparation by anionic exchange allows the preparation of the same tetrahedral W species at high loadings. The comparison of several point analysis also shows that the homogeneity of the preparation is good when using anion exchange, and much less ideal when using impregnation.

Table 4
Amount of NH_3 irreversibly adsorbed by different samples

Sample (calcination temperature)	wt% W	NH_3 adsorbed	
		mmol/g	mol/mol W
ZW_I (1073)	19.1	0.13	0.12
$ZW_{0.1}$ (873)	19.4	0.26	0.25
Zr-1 (873)	20.6	0.35	0.33
Zr-1 (1073)	i.d.	0.32	0.30

3.5. *Acidity of the samples*

Changes of coordination are expected to induce changes in acidity and therefore acidity was determined by NH_3 and pyridine adsorption. The results for ammonia are reported in Table 4 for samples calcined at different temperatures. The number of sites decreases slightly after calcinations above 1073 K. The exchanged samples retain a high number of acid sites, which may simply be a result of a better dispersion of W and higher resistance against sintering.

The Lewis/Brønsted character of the acid sites was investigated by pyridine adsorption. Pyridine forms both pyridinium and coordinated species, stable up to 573 K (not shown). The situation is the same for the impregnated sample.

The conclusion of the study of preparation and characterization is therefore that peroxotungsten species can be exchanged onto zirconia. The peroxo species decomposes into a tetrahedral oxotungsten, which remains isolated even at high concentration at low temperatures and is converted to isopolytungstates upon calcination at high temperature. The W surface sites are more acidic than the corresponding W oxides for two reasons: a better dispersion of W related to the strong interaction with the surface and a low coordination of the W cations.

3.6. *Catalytic properties for dibenzothiophene oxidation*

The oxidation of dibenzothiophene by hydrogen peroxide was investigated using the samples supported by the commercial zirconia (Table 2), dried at 373 K and showing the tetrahedral symmetry. The reaction of DBT with H_2O_2 yields the corresponding sulfone with high selectivity. In acetonitrile as solvent, the reaction is fast at 333 K (Fig. 6) and full conversion is observed in a few minutes using 5 mmol H_2O_2 for 0.5 mmol DBT, 0.1 g catalyst in 10 ml of acetonitrile as solvent. A partial decomposition of H_2O_2 into O_2 is also noted. The selectivity to O_2 has been reported on the curves of Fig 6: it decreases from 94% for the Zr-2 sample, to 57% for Zr-1 of higher W content. It is well known that bases catalyze the formation of imminoperacids by reaction of H_2O_2 on acetonitrile, and the further decomposition of H_2O_2 [37]. The higher decomposition of H_2O_2 at low W content is therefore attributed to the well-known basic character of ZrO_2 [31] attested here by the presence of carbonates at the surface for low W contents. Mg-rich hydrotalcites which are weak bases show the same behavior

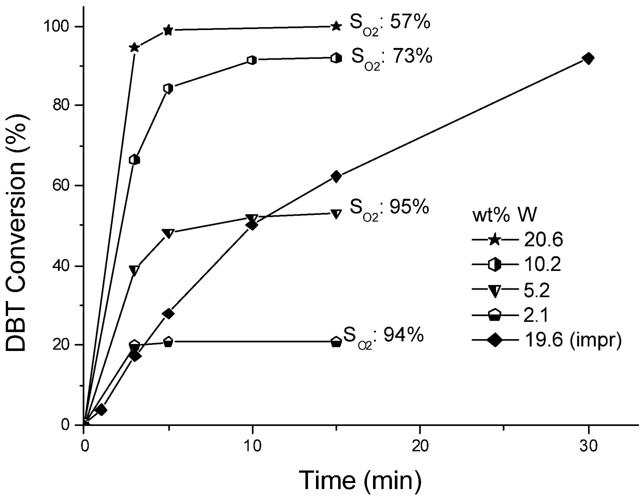

Fig. 6. Conversion as a function of time at 333 K for W–ZrO_2 with different contents using a ratio $DBT/H_2O_2 = 10$ and acetonitrile as solvent.

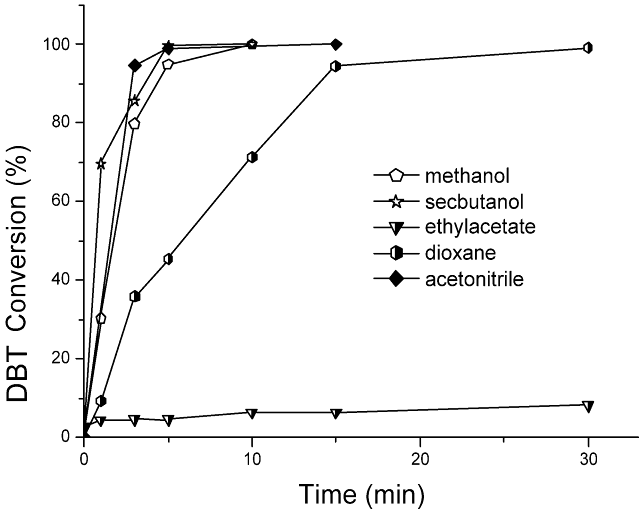

Fig. 7. Effect of solvents on the oxidation of DBT by hydrogen peroxide on WZr-1 at 333 K with a ratio $DBT/H_2O_2 = 10$.

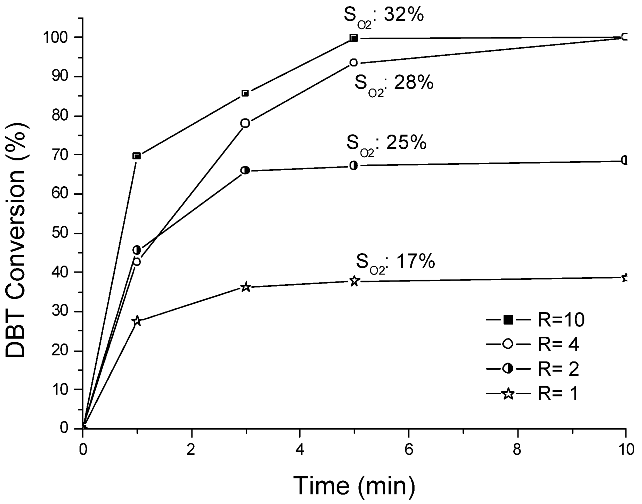

Fig. 8. Influence of the ratio H_2O_2/DBT on the conversion of dibenzothiophene at 333 K on WZr-1 and *sec*-butanol as solvent.

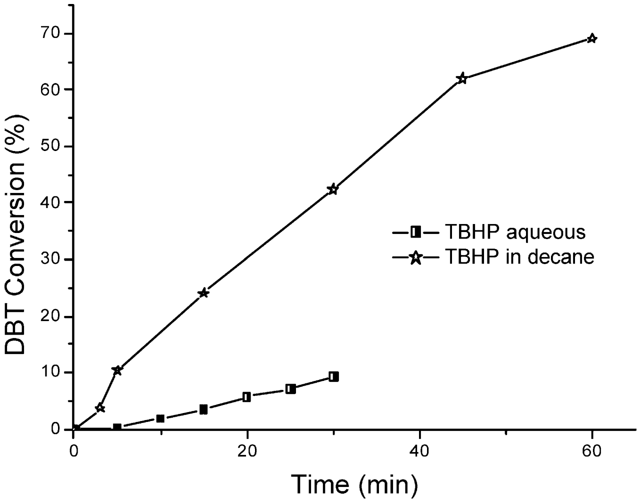

Fig. 9. Oxidation of dibenzothiophene by *tert*-butylhydroperoxide dissolved in water or decane at 333 K using WZr-1 as catalyst.

and catalyze both the oxidation of DBT to sulfone at a much slower rate and H_2O_2 decomposition [38]. The coordination of W has a strong influence on the reaction rate since the impregnated sample tested with the $H_2O_2/DBT = 10$ exhibits a much lower activity.

The effect of the solvent was investigated with the same H_2O_2/DBT ratio $R = 10$ at 333 K, and WZr-1 as catalyst. The results reported in Fig. 7 show that acetonitrile, methanol, or 2-butanol are nearly equivalent, 1,4-dioxane decreases slightly the reactivity and acetyl acetate is not acceptable. The solvent has a significant influence on the selectivity for O_2 formation: the best solvent from this point of view would be dioxane (12% loss into oxygen), then methanol (22%), butanol (32%), and ethyl acetate (38%). In methanol, or 2-butanol sulfone is insoluble and crystallizes in small white particles which can be easily separated by filtration. The reaction also works well in a mixture acetonitrile/decane (5.2 ml acetonitrile + 5 ml decane) as solvent: in this case full conversion is obtained after 15 min.

The kinetics of DBT oxidation was investigated varying the amount of H_2O_2 (Fig. 8). While the reaction on DBT is first order relative to H_2O_2, the decomposition of H_2O_2 into O_2 is a bimolecular reaction and the selectivity to oxygen decreases from 32% at $R = 10$, to 17% at $R = 1$. The conversion observed after 5 min for the experiment with $R = 1$ reaches 38%, not far from the 46.5% corresponding to the stoichiometry of the reaction; therefore, the decomposition of H_2O_2 controls the rate.

The oxidation of DBT can also be performed with *tert*-butylhydroperoxide as oxidizing agent (Fig. 9), with a slower rate compared to H_2O_2, as is usually observed in many oxidations. In that case a lower conversion is obtained using TBHP in aqueous solution compared to TBHP in decane showing that the reaction is severely inhibited by water.

Table 5
Recycling of WZr-1 catalyst using a ratio $\mathrm{DBT}/\mathrm{H_2O_2} = 10$ and acetonitrile as solvent

Experiment	Conversion at 10 min (%)	Weight of catalyst (g)	Specific rate constant ($\mathrm{min^{-1}\,g^{-1}}$)
1	78	0.3	0.30
2	67	0.24	0.27
3	50	0.18	0.31

The recyclability of the catalyst sample was measured on WZr-1 using a ratio of reactants $\mathrm{H_2O_2}/\mathrm{DBT} = 10$. This experiment was done by filtering the catalyst at the end of the reaction, then adding a new reactant feed. The rate was determined by computing the first order rate constant at the different steps: upon recycling, a lower conversion after 10 min was noticed, but the corresponding specific rate constant was retained within experimental error (Table 5). The sample has not then been appreciably modified by the reaction medium, but fine particles were lost in the filtration, resulting in a lower conversion.

In conclusion, the oxidation of dibenzothiophene by H_2O_2 or TBHP is efficiently catalyzed by tetrahedral W catalysts. This effect is quite consistent with earlier work in which the activity for epoxidation was related to the acidity of transition metal compounds [39]. Indeed the situations are similar since in both cases radical mechanisms leading to decomposition of the oxidizing agents have to be avoided. The reaction is sensitive to solvent effects but can be performed either in decane with TBHP or 2-butanol with H_2O_2. These solvents are not toxic and could be used at the industrial scale. The activity of these catalysts is higher than that of titano-silicates and the selectivities are comparable.

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