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V-, Mo- and W-containing layered double hydroxides as effective catalysts for mild oxidation of thioethers and thiophenes with H_2O_2

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ABSTRACT

Catalytic oxidation of thioethers and thiophene derivatives with H_2O_2 was performed at 40 °C and atmospheric pressure, in presence of W-, V- and Mo-containing layered double hydroxides (LDH). The catalysts were prepared by direct ion exchange with metal-oxoanions, i.e. WO_4^{2-}, $W_7O_{24}^{6-}$, $V_2O_7^{4-}$, $V_{10}O_{28}^{6-}$, MoO_4^{2-} and $Mo_7O_{24}^{6-}$, of the LDH containing aluminum and magnesium atoms in the brucite layer. All the catalysts showed good activity and selectivity in the sulfoxidation reaction, but the catalyst performances strongly depended on the nature of the anion species intercalated in the interlayer gallery. Thus, the W-based LDH was more active and more stable than the V-LDH and Mo-LDH catalysts. The conversion of sulfur-containing compounds is also dependent on the nucleophilicity of substrates and the following order of reactivity was observed benzothiophene < dibenzothiophene < diphenyl-sulfide < benzyl-phenyl-sulfide < methyl-phenyl-sulfide.

1. Introduction

One of the most important reasons which stimulate research in the field of the catalytic sulfoxidation reactions is the removal of sulfur compounds from fuels and industrial effluents, in order to satisfy the new environmental legislations [1]. Indeed, the catalytic oxidative desulfurization (ODS) can be considered a promising alternative technology to the current hydrodesulfurization process for reducing sulfur in gasoline and diesel fuels [2–5]. In the ODS process, the sulfides and thiophene derivatives are converted into their corresponding sulfoxides and sulfones, which are preferentially extracted due to their increased polarity. These reactions are carried out in liquid phase, under mild conditions, in the presence of oxidizing agents, such as organic peroxyacids, peroxides, hydroperoxydes, and hydrogen peroxide.

The hydrogen peroxide is mostly chosen as oxidizing agent owing to its high effective-oxygen content (47%), cleanliness (it produces only water as by-product) and acceptable safety in storage and operation (the use, storage, and transportation of higher concentrations of H_2O_2 than ~60% are not desirable for safety reasons). Therefore, in the last years the importance of hydrogen peroxide as "green" oxidizing agent for liquid-phase organic reactions has grown considerably [6–8] and the catalytic oxidation of sulfur-containing compounds by H_2O_2 was intensely studied.

Some promising heterogeneous systems such as Ti-containing zeolites (TS-1, Ti-beta) [9–11], Ti-hexagonal mesoporous silica [11–13], V- or Mo-containing molecular sieves [14,15], supported oxides V_2O_5/Al_2O_3 [16] or solid bases like hydrotalcites [17–19] were used for the selective oxidation of sulfur-containing compounds (sulfides, sulfoxides or thiophenes) by H_2O_2.

We recently reported that layered double hydroxides with Mg^{2+} and Al^{3+} cations in the brucite-like layer and tungstate and *para*-tungstate anions in the interlayer gallery are active catalysts for the oxidation of S-containing compounds [20] and dimethylsulfoxide [21] with H_2O_2. The aim of this work was to prepare and characterize new LDH-based catalysts, like MgAl-LDHs exchanged with anionic V- and Mo-species and to compare their catalytic performances with those of the W-containing LDH materials in the organic sulfur compounds oxidation with H_2O_2. The oxidation reaction was performed in both two-phase liquid–solid and three-phase liquid–liquid–solid systems, in order to obtain information on the applicability of this reaction for the oxidative desulfuration of hydrocarbon mixture or fuels.

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2. Experimental

2.1. Catalysts preparation

The parent MgAl-LDH (denoted MA-NO_3) was prepared by pH controlled co-precipitation of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$, according to the method reported previously [20]. Me-containing LDH catalysts (Me = W, V, Mo), denoted as W-LDH, V-LDH and Mo-LDH, were obtained by direct ion exchange of the crystalline MA-NO_3 material, using $Na_2WO_4 \cdot 2H_2O$, $NaVO_3$ and $Na_2MoO_4 \cdot 2H_2O$, respectively. In order to prepare the W-LDH sample, 3 g of MA-NO_3 was suspended in 75 ml decarbonated water previously purged by nitrogen. This suspension was stirred at 70 °C and under nitrogen flow for 1 h, and then a solution of 2.18 g $Na_2WO_4 \cdot 2H_2O$ dissolved in 150 ml decarbonated water was added. The mixture was maintained at 70 °C and nitrogen flow for 3 h and the pH value was monitored and maintained constant at 9.5 (with NaOH 0.1 M). The resulting products were filtered, washed thoroughly with deionized and decarbonated water and dried overnight at 40 °C.

V-LDH sample was prepared by direct ion exchange of MA-NO_3 with vanadate anions at 55 °C, according to the method reported by Dula et al. [22]. A portion of 3 g of MA-NO_3 was suspended in 75 ml decarbonated water previously purged by nitrogen. This suspension was stirred at 55 °C and under nitrogen flow for 1 h, and then a solution of 1.83 g $NaVO_3$ dissolved in 150 ml decarbonated water was added. The mixture was maintained at 55 °C and nitrogen flow for 1 h. During the exchange period, the pH was dropped and maintained constant at the value of 4.5 by adjusting with HNO_3 0.1 M. The resulting products were filtered, washed thoroughly with deionized and decarbonated water and dried overnight at 40 °C.

Mo-LDH sample was prepared by exchange with molybdate anions at 60 °C, according to the method reported by Carriazo et al. [23]. 3 g of MA-NO_3 was suspended in 75 ml decarbonated water previously purged by nitrogen. This suspension was stirred at 60 °C and under nitrogen flow for 1 h, and then a solution of 4.05 g $Na_2MoO_4 \cdot 2H_2O$ dissolved in 150 ml decarbonated water was added. The mixture was maintained at 60 °C and nitrogen flow for 5 h. During the exchange period, the pH was dropped and maintained constant at the value of 4.5 by adjusting with HNO_3 0.1 M. The resulting products were filtered, washed thoroughly with deionized and decarbonated water and dried at 40 °C.

2.2. Catalyst characterization

All the catalysts were used as such for characterizations and sulfoxidation reaction. Adequate physicochemical techniques (chemical analysis, X-ray diffraction, DRUV spectrometry, thermogravimetric analysis (TGA) and nitrogen sorption) were used to evaluate the textural and morphological properties, as well as to confirm the presence of the metal-anion species in the intercalated state within the gallery of LDH samples. The chemical composition was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES; LIBERTY 200, VARIAN spectrometer) after the digestion of the sample with nitric acid solution. Powder XRD patterns were collected on a Bruker AXS D8 diffractometer using Cu Kα radiation. The nitrogen adsorption/desorption isotherms (−196 °C) were measured with a Micromeritics ASAP 2010 automatic analyzer. UV–vis diffuse reflectance spectra were recorded on a Varian Cary 05 E UV–vis–NIR spectrometer equipped with an integrating sphere using $BaSO_4$ powders as the reflectance standard. Thermogravimetric analysis was carried out in a Netzsch TG 209C thermobalance. About 15 mg of catalyst was loaded, and the airflow used was 50 $cm^3\ min^{-1}$. The heating rate was 5 °C min^{-1} and the final temperature was 900 °C.

2.3. Typical procedure for oxidation in liquid–solid system

The catalytic experiments were carried out at atmospheric pressure in a three-neck glass batch reactor (50 ml), equipped with magnetic stirrer, thermometer, and condenser, immersed in a thermostated oil bath. In a typical run, the solid catalyst (50 mg) was suspended under stirring (800 rpm) in a mixture containing 1 mmol of organic substrate, 5 mmol of hydrogen peroxide (30 wt.% aqueous solution), and 10 ml solvent. Blanc experiments were carried out mixing the reactants in absence of catalyst. Samples of the reaction mixture were periodically withdrawn, filtrated and analyzed on a Varian 3900 chromatograph equipped with a capillary column (DB-1, 60 m, 0.20 mm i.d., 0.25 μm film thickness). The hydrogen peroxide concentration was measured by standard iodometric titration.

3. Results and discussion

3.1. Characterization of catalysts

The successful intercalation of the oxoanions species in the interlayer gallery, as well as the physicochemical characteristics of solids were investigated by using various techniques.

The results of the elemental analysis are summarized in Table 1. The atomic Mg^{2+}/Al^{3+} ratio in MA-NO_3 corresponds to that of the nitrate solutions used for coprecipitation, which was 2:1. For the W-LDH sample, obtained by ion exchange at pH 9.5, this ratio was also very close to the value existing in the precursor. On the contrary, for V- and Mo-LDHs the Mg^{2+}/Al^{3+} ratio strongly decreased after the ion exchange process, probably due to the extraction of Mg^{2+} cations in acid solutions (for instance, the ion exchange for molybdate anions was carried out at pH of 4.5). On the other hand, the amount of

Table 1
Main characteristics of LDH samples

Sample	Mg/Al/Me[a] (atomic ratios)	UV bands (nm)	Oxospecies		S_{BET} (m^2/g)	Weight loss 250–500 °C (%)[b]
			Nature	%		
MA-NO_3	2.00/1.00		–		16	35.8
W-LDH	1.99/1.00/0.5	220 260	WO_4^{2-} $W_7O_{24}^{6-}$	71 29	25	17.6
V-LDH	1.43/1.00/0.7	310 430	$V_2O_7^{4-}$ $V_{10}O_{28}^{6-}$	30 70	50	11.5
Mo-LDH	1.6/1.00/0.6	255 325	MoO_4^{2-} $Mo_7O_{24}^{6-}$	39 61	45	13.8

[a] Me = W, V or Mo.
[b] By TGA.

nitrogen in the W-, V- and Mo-intercalated LDHs was lower than 0.3%, indicating that the initial nitrate anions were largely exchanged with metals-containing anions.

The UV–vis spectra of the parent LDH and modified LDH samples indicated that the ion exchange process generated significant modifications of the initial material. Thus, large absorption bands in the range of 250–500 nm appeared in the UV spectra of the W-, V- and Mo-containing LDHs. These spectra were deconvoluted (using Gaussian curves) and two bands were identified for each metal, proving the intercalation of two main oxoanions species. According to the literature [18,22,23] the UV bands were attributed to different oxospecies, and they are summarized in Table 1. The percents of the anionic species were calculated and included in this table.

The textural properties of parent hydrotalcite were significantly changed upon the exchange process with oxometalates anions. Thus, the BET specific surface areas of W-LDH, V-LDH and Mo-LDH are 25, 50 and 45 $m^2 g^{-1}$, while for the parent MA-NO_3 it is only 16 $m^2 g^{-1}$ (Table 1). The N_2 adsorption–desorption isotherms (not shown) indicated that the pore volumes for the W-, V- and Mo-intercalated LDH were also greater that that of the precursor.

In thermogravimetric analysis, the parent and oxometalates-containing LDH samples exhibited two important stages of weight loss, which are characteristic for the layered double hydroxides. The first stage, between 30 and 250 °C (which is obviously attributed to the removal of interlayer water molecules and adsorbed water molecules) was around 14.0% for all the materials. For the parent layered double hydroxides (MA-NO_3 sample), a second stage high weight loss is recorded between 250 and 500 °C, and it corresponds to the dehydroxylation of brucite-like layers and the decomposition of nitrate ions. This weight loss is nearly three times larger than those obtained for the exchanged LDHs (Table 1). In fact, the weight loss observed for the exchanged LDH samples (250–500 °C) corresponds to the dexydroxylation of the brucite-like layers, the removal of residual nitrate ions and especially to the decomposition of metal-containing anions into metal oxides (which remain in the solid phase).

The XRD patterns for the exchanged LDH materials are shown in Fig. 1, together with that of the unchanged sample. The parent MA-NO_3 sample exhibited patterns characteristic of the well-crystallized layered structure of hydrotalcite-like type material, with a basal spacing of 8.9 Å.

The XRD patterns of the exchanged LDHs show that the basic lamellar structure of the host solid was kept, but the basal distances increased, confirming the replacement of smaller nitrate anions by larger anion species. The basal spacing, calculated from the reflection of [0 0 3] plane are 10.46, 10.2 and 11.5 Å, for the W-LDH, V-LDH and Mo-LDH, respectively. They agree to the previous reported data [20,24,25]. Simultaneously, some structural disorder was observed, the XRD patterns of intercalated materials showing a broad spread of reflections. This indicates that there are at least two intercalating species into the interlayer region. Moreover, two new sharp reflections were observed in the XRD pattern of V-LDH sample obtained by ion exchange in acid solution. These reflections could be attributed to a polyoxometalate salt impurity formed by reaction of the cations from the partially dissolved brucite layer with the polyoxoanions used for intercalation or to a defect LDH structure resulting from acid damage, as previously reported [26,27].

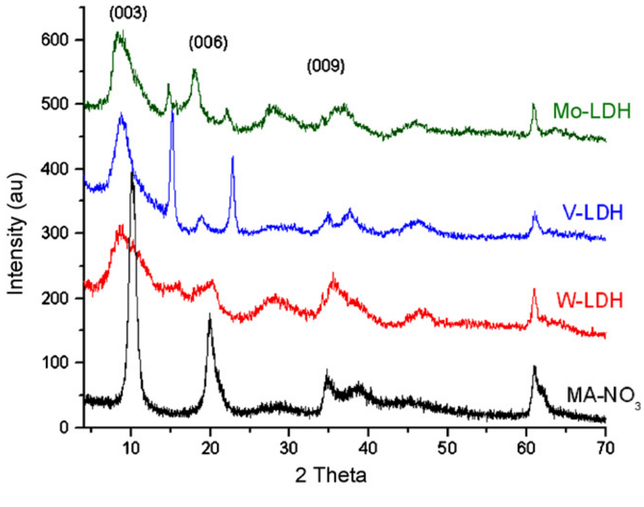


Fig. 1. X-ray diffraction patterns of MA-NO_3 and exchanged LDHs.

3.2. *Oxidation of model S-containing compounds in two-phase solid–liquid system*

The catalytic activity of the modified LDHs (described above) was studied in the oxidation of the organic sulfides and thiophene derivatives, which are the major sulfur-containing compounds present in fuels. Bulky compounds, such as: methyl-phenyl-sulfide (MPS), benzyl-phenyl-sulfide (BPS) and diphenyl-sulfide (PPS), benzothiophene (BT) and dibenzotiophene (DBT) were selected as model molecules. The oxidation reaction has been carried out using dilute hydrogen peroxide (aqueous solution, 30%), at 40 °C, in the presence of acetonitrile as solvent. The organic solvent forms a single phase with the substrate and hydrogen peroxide solution. Under these conditions, the oxidation reaction of sulfides led to the corresponding sulfoxides and sulfones as major products (Scheme 1, Eq. (1)).

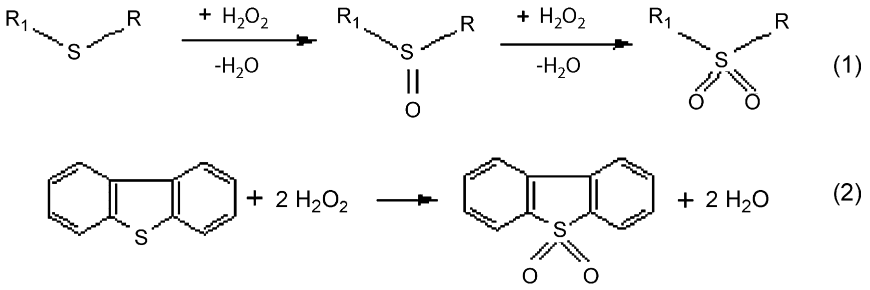
On the contrary, the kinetic profile of the thiophenes oxidation indicated only the formation of corresponding sulfones, even for low levels of conversion of substrate (Scheme 1, Eq. (2)).

The direct decomposition of hydrogen peroxide $H_2O_2 \rightarrow H_2O + {}^1/_2O_2$ was observed during the oxidation process, but the efficiency of H_2O_2 (defined as 100 × mole of H_2O_2 consumed in the formation of sulfones/mole of H_2O_2 converted) was higher than 95% for all the oxidation tests.

The results obtained in the organic sulfur compounds oxidation at 40 °C, without catalyst (w.c.) and using fresh W-LDH, V-LDH, Mo-LDH and MA-NO_3 samples as catalysts, in acetonitrile as solvent, are plotted in Fig. 2. The blank experiments performed in absence of catalyst showed very low conversions for both organic sulfures and thiophenes.

Low conversions (1–11%) were also obtained in the presence of the MA-NO_3 sample which does not contain oxometalates species. The conversion of organic sulfur compounds substantially increased when exchanged LDH materials were used as catalysts, showing that the W, Mo and V-oxospecies have an essential contribution to the activation of the oxidizing agent. For example, conversions above 100% were obtained in the MPS oxidation over Mo-LDH and W-LDH catalysts after only 45 min of reaction. However, as it can be seen in Fig. 2, the conversion strongly depends on the metal nature (of course, in relation to the catalytic species). For the same amount of catalyst and reaction time, the order of the catalytic performance was: W-LDH > Mo-LDH > > V-LDH.

In order to explain these differences in catalytic activity, two main aspects have to be considered: (i) the intrinsic nature of active sites (metal and oxospecies nature) and (ii) the distribution and concentration of oxospecies. In the first case, from UV data (Table 1) it was observed that for all the catalysts, the ratio between the tetrahedral and octahedral species was about 70/30,



Scheme 1.

but from the XRD data resulted that vanadium could be involved in the formation of some complex species (at $2\theta = 15$ and 22°) which probably have no catalytic activity. The second aspect can be related to the accessibility of reacting molecules to the active sites. For example, BET data indicated higher surface for V-LDH than W-LDH, at approximately the same *d*-spacing (this suggests the same accessibility of reagent molecules to the active sites); however, W-LDH is about two-fold more active. Consequently, it results that the intrinsic nature of catalytic site has the main influence for these reaction systems.

The results plotted in Fig. 2 showed that the model molecules were oxidized at different rates. The relative reactivity of various organic sulfur compounds was similar on all catalysts and the observed reactivity sequence (BT < DBT < PPS < BPS < MPS) parallels the electron density (nucleophilicity) at the sulfur atom in each of these compounds, in accord with the previous results [28,29]. Moreover, the high conversions of the sulfur-containing substrates suggest a very good accessibility inside of the porous structure of the Me-LDH catalysts for these large molecules.

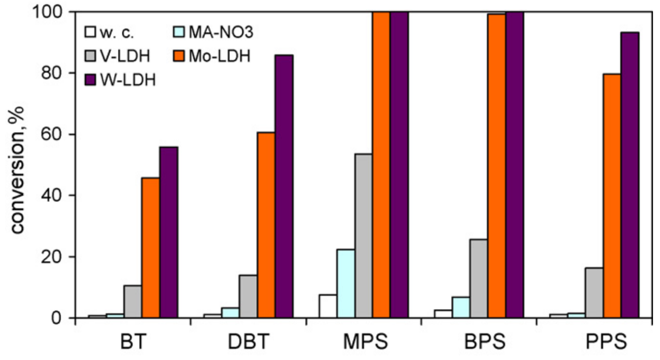


Fig. 2. Effect of the catalyst on the organic sulfur compounds conversion; $T = 40$ °C, H_2O_2/substrate = 5 (mol/mol); Solvent = MeCN, $t = 45$ min for MPS, BPS and PPS, $t = 3$ h for DBT and $t = 18$ h for BT.

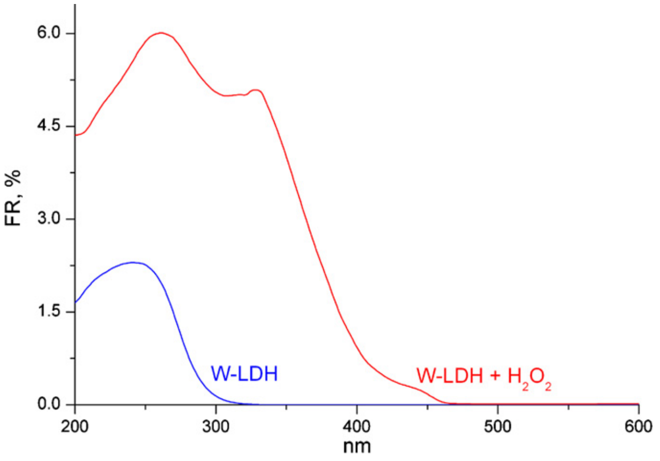


Fig. 3. UV–vis–DR spectra of W-LDH before and during the oxidation reaction with H_2O_2.

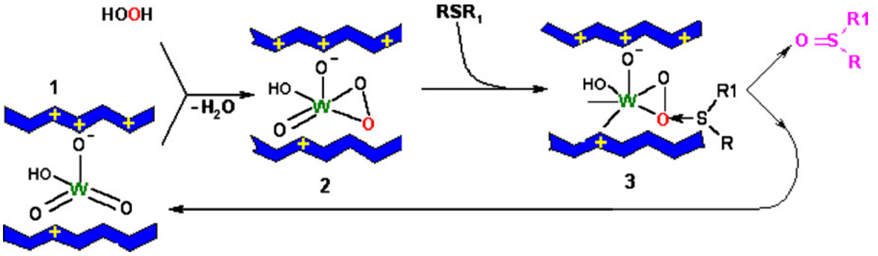
A plausible catalytic cycle for the oxidation of sulfides to sulfoxides, which is the first stage of the oxidation process, over W-containing LDH catalyst, is depicted in Scheme 2. As known, the role of the metal atom (W, V or Mo) is to form peroxo-metal species which are able to activate the H_2O_2 molecule. This mechanism involves in the first step the easy formation of the peroxotungstate species (**2**) after the interaction of the tungstate anion (**1**) with the hydrogen peroxide. Direct evidence of the formation of such reactive intermediates is provided by the modification observed when the H_2O_2 was added on the W-LDH catalyst. First, the solid color changed instantly from white to orange-brown.

Moreover, and important modifications in the UV–vis spectrum appeared (Fig. 3). Thus, the λ_{max} shifted from 250 nm (in W-LDH) to 325 nm (in H_2O_2-W-LDH), confirming the formation of the peroxotungstate species.

This species facilitates the transfer of the electrophilic oxygen to sulfide (**3**), forming the sulfoxide. Consequently, the nucleophilicity of substrate has an important role and thus the order of reactivity mentioned above could be explained.

As concerns the second type of catalytic species, it is well known that the peroxo bridged high-nuclearity metal species are convincingly proved to be less active toward oxygen atom transfer than the lower nuclearity species [30]. Though these species have more metal atoms (e.g., $W_7O_{24}{}^{6-}$ or $Mo_7O_{24}{}^{6-}$), however only terminal Me=O bonds are able to form easier peroxo rings. That means about 30% percent of the catalytic species are less active, if the results from DR-UV measurements are taken into account. Moreover, as approximately all the vanadium-containing species have at least two metal atoms or more ($V_2O_7{}^{4-}$ and $V_{10}O_{28}{}^{6-}$), the V-LDH is lesser active than the other two LDH-based catalysts.

In order to evaluate the stability and leaching tendency of the anionic species in the LDH matrix, the W-LDH, V-LDH and Mo-LDH samples were used in four 45 min catalytic cycles of MPS oxidation with H_2O_2. The catalyst was separated by filtration after each cycle, washed with solvent and then placed into a fresh reagent mixture. Over W-LDH and V-LDH catalysts, the MPS conversion remained almost constant for the four catalytic cycles. On the contrary, the Mo-LDH catalyst loses its activity after each cycle of reaction (from 100% after the first run to 75% after the four run). This loss may be attributed to Mo-anionic species leaching from the solid. In order to test this assertion, after the first cycle the mixture was separated by filtration and the reaction between MPS and H_2O_2 was carried out using the clear solution. In this case, 35% of MPS was converted into sulfone, suggesting that an important amount of Mo-species was leached and these species catalyze the oxidation reaction in solution.



Scheme 2. Proposed mechanism for the sulfide oxidation with H_2O_2 over W-LDH catalyst.

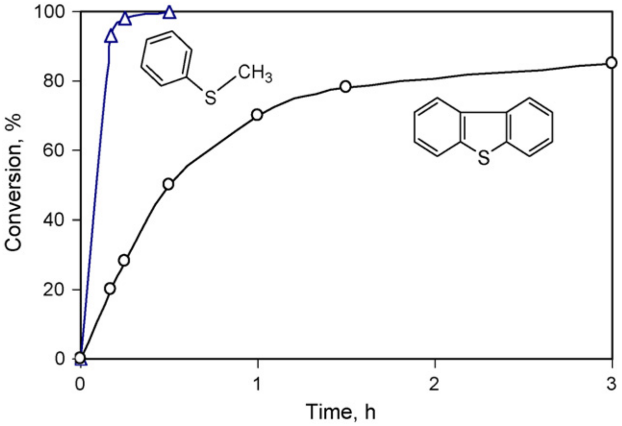


Fig. 4. Kinetics of MPS and DBT sulfoxidation in three-phase L–L–S system. $T = 40\ ^\circ C$. Catalyst: W-LDH.

3.3. Oxidation with simultaneous extraction: three-phase L–L–S reaction system

Oxidative desulfurization of a synthetic fuel, consisting of the MPS or DBT dissolved in *n*-decane was carried out at 40 °C, under agitation, in three-phase liquid–liquid–solid system: an organic layer (*n*-decane (L)), an aqueous layer containing a polar solvent (acetonitrile) and 30% H_2O_2 (L) and the catalyst (S), dispersed in the liquid phases. Initially, more than 95% of the S-containing compound was identified in *n*-decane. The main role of the polar solvent is to solve the aqueous H_2O_2 solution (immiscible with the *n*-decane). Moreover, during the chemical treatment, the oxidized organic sulfur compounds (immiscible with the *n*-decane) transfer integrally in acetonitrile. The oxidized product can therefore be removed by a simple liquid–liquid separation. For a typical run, 1.5 ml of 30% aqueous hydrogen peroxide was mixed with 10 ml of acetonitrile and 100 mg of W-LDH catalyst. Then 20 ml of *n*-decane containing 1.8 mmol of organic sulfur compounds (MPS or DBT) was added, and this three-phase mixture was heated at 40 °C with stirring. Concentrations of the initial and oxidized products in the two liquid phases were periodically determined by GC.

The kinetic profiles of the oxidation reaction of MPS and DBT (Fig. 4) show that the W-LDH catalyst exhibits remarkably high activity in the conversion of both sulfides and thiophenes. Moreover, this catalyst showed excellent hydrogen peroxide efficiency (more than 95%) for the sulfoxidation reaction. Using this oxidation/extraction technique, with this catalyst, under very mild conditions (40 °C, atmospheric pressure) about 85% of DBT (after 3 h) and 100% of MPS (after only 45 min) were removed from *n*-decane phase.

4. Conclusions

Intercalation of oxometalates ions in the LDH structure has been successfully realized by direct anionic exchange, as confirmed by XRD, N_2 adsorption, TGA and DR-UV spectroscopy. Most of the initial nitrate ions from LDH precursors were easily exchanged by W-, V- and Mo-containing species. Intercalation led to an increase in basal spacing, surface area and micro- and mesoporous volume. W-, V- and Mo-containing layered double hydroxides exhibited very good catalytic potential for the oxidation of organic sulfur compounds with dilute H_2O_2 aqueous solution, at moderate temperature, in both two- and three-phase system. The oxidation/extraction process leads to removal of a substantial amount of the sulfur from a synthetic fuel.

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