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Heterogeneous sulfoxidation of thioethers by hydrogen peroxide over layered double hydroxides as catalysts

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Abstract

A new method for mild oxidation of thioethers with hydrogen peroxide in heterogeneous catalysis is described. The layered double hydroxides (or hydrotalcite-like materials) act as basic catalysts for the sulfoxidation reaction with hydrogen peroxide in the presence of acetonitrile. The influence of the nature of thioether, the type of catalyst, the reaction temperature and reaction time on the catalytic activity and selectivity in this reaction has been investigated. A mechanism of the sulfoxidation reaction is proposed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Sulfoxidation reaction; Thioether; Catalytic activity; Hydrogen peroxide; Acetonitrile

1. Introduction

The interest of sulfoxides and sulfones in fine organic synthesis is well known, due to their increasing use as agrochemicals, pharmaceutical products, lubricants, etc. Sulfoxides are formed by partial oxidation of sulfides, and, upon further oxidation, are converted to sulfones (Scheme 1).

Hydrogen peroxide, either alone or associated with various solvents or catalysts, is the most widely used agent for oxidizing organic sulfides [1]. In the last years, H_2O_2 has received attention because of its environmental implication, water being the only by-product of the oxidation reaction.

The transition-metal (Ti, Mo, Fe, V, W, Re, Ru) complexes are active catalysts for the selective oxidation of thioethers by H_2O_2 in homogeneous conditions. More recently it has been shown that some metals (Ti, V), incorporated in a zeolitic framework, are able to catalyze such an oxidation reaction under mild conditions [2,3].

In a series of recent papers it has been reported that other solid catalysts, such as layered double hydroxides (LDHs), are able to catalyze the H_2O_2 oxidation of olefins [4–6] as well as of phenol [7]. Until now, to our knowledge, there is no report concerning the oxidation of sulfur compounds by hydrogen peroxide using LDHs as catalysts. In this study, we investigated the thioethers sulfoxidation with H_2O_2, using Mg/Ni/Al-LDHs as catalysts, and acetonitrile as solvent.

2. Experimental

Materials. Thioethers (>97%) from Aldrich were used as supplied. Hydrogen peroxide (aqueous solution 30 wt.%) was obtained from Proabo. Acetonitrile,

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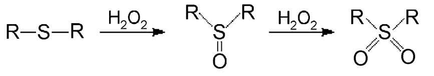


(1)

Scheme 1.

99% (Aldrich) and acetone, analytical grade, were used as solvent.

Catalysts. Hydrotalcite compounds (HT) with different Mg/Ni/Al molar ratios were synthesized by precipitation under low supersaturation wherein both the precipitants (NaOH and Na_2CO_3) and the corresponding metal nitrates are added slowly and simultaneously holding the pH constant. The resulting precipitate was hydrothermally treated in a Teflon-coated autoclave at 453 K for 12 h. The resulting solid was isolated, washed with deionized water and dried overnight at 353 K. X-ray diffraction patterns were recorded on a CGR Theta diffractometer using Cu Kα radiations ($\lambda = 0.15401$ nm). Scans were performed over the 2θ range from 6 to 70°. Thermogravimetric and calorimetric experiments were carried out on a Setaram TG DSC 111 apparatus under a flow of nitrogen gas. The temperature was increased at a rate of 1 K/min from 303 to 1173 K. BET-N_2 surface areas were determined on a Micromeritics ASAP 2000 instrument.

Catalytic experiments. The catalytic sulfoxidation of thioethers was carried out in a glass flask equipped with a magnetic stirrer, a thermometer and a condenser. In a typical experiment, HT (100 mg) was stirred with sulfide (1 mmol), the solvent (20 ml) and H_2O_2 (2 ml) at a constant temperature. Samples were periodically collected and analyzed by GC. The hydrogen peroxide was measured by standard iodometric titration.

3. Results and discussion

3.1. Characterization of the Ni:Mg:Al-LDHs

As it is known, there are several methods for the synthesis of LDHs, but among them the precipitation at low supersaturation is largely used [8]. Obviously, the fresh precipitate can be aged at 338 K for several hours or it can be hydrothermally treated. Generally, the hydrothermal treatments are applied to freshly precipitated mixed hydroxides in order to transform the small crystallites into larger and well-crystallized ones and to transform amorphous precipitate into LDHs.

For the synthesis of our LDHs the hydrothermal treatment of the fresh precipitate was applied, and a well-crystallized material was obtained, as it can be seen from SEM images (Fig. 1) by comparison with the conventional method.

On the other hand, the difference between the two methods of precipitate aging is very well illustrated by their XRD patterns, Fig. 2. The sample obtained by hydrothermal treatment has a high degree of crystallinity.

XRD of the samples (Fig. 3) indicated the formation of LDH single phase for all compositions, and exhibited sharp and symmetric reflections for (0 0 3), (0 0 6), (1 1 0) and (1 1 3) planes and broad and asymmetric reflections for (1 0 2), (1 0 5) and (1 0 8) planes characteristic of LDHs (hydrotalcite JCPDS 22-70 and takovite JCPDS 15-87).

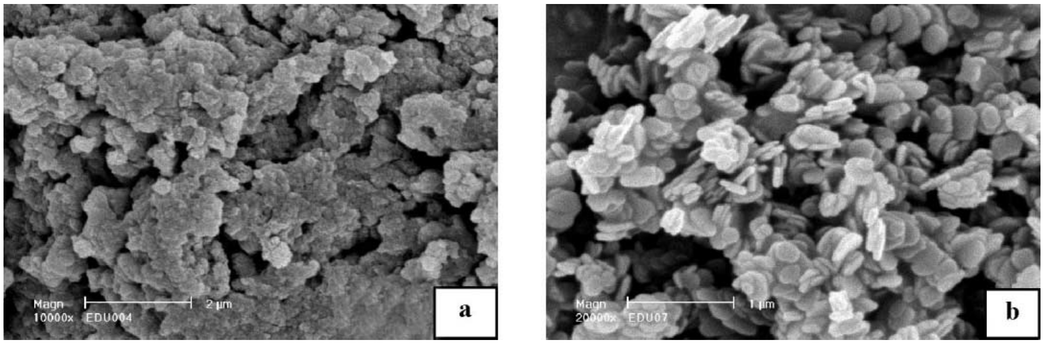


Fig. 1. SEM images of Ni:Mg:Al (1:1:1)-LDHs obtained by conventional (a) and hydrothermal aging (b).

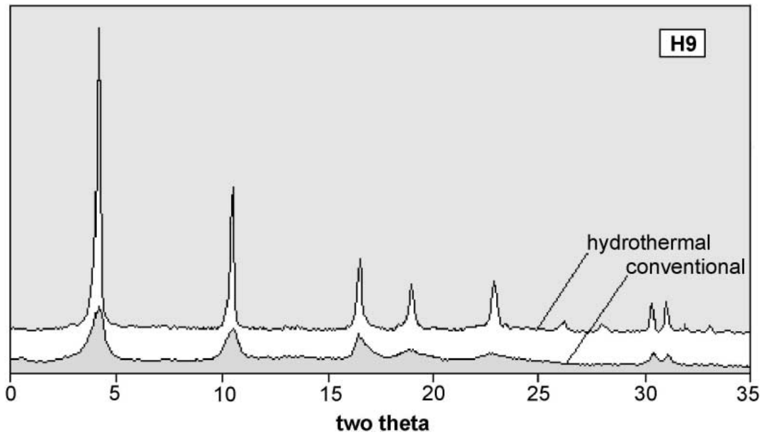


Fig. 2. XRD pattern for Ni:Mg:Al (1:1:1)-LDHs obtained by conventional (a) and hydrothermal aging (b).

The small differences in the intensity of reflections (see (0 0 6) plane) on going from one sample to another indicate that their crystallinities are close to each other.

The LDH samples were calcined at 523 K under vacuum to remove the adsorbed water. Though a substantial dehydration of the gallery surface occurred, the layered structure is maintained, as it was observed from XRD patterns. The surface area of the calcined samples are situated in a narrow range 53–63 m^2/g, except H4 (MgAl-LDH), thus it could be assumed that the LDH samples have relatively similar crystal sizes, Table 1. From the same table, it can be observed that the weight loss decreases with the increase of nickel content in the Brucite-like layer.

3.2. The oxidation of thioethers

The catalytic activity of the LDHs described above was studied in the oxidation of various thioethers under different reaction conditions. The oxidation reaction has been carried out using diluted hydrogen peroxide (30 wt.% in water) in the presence of

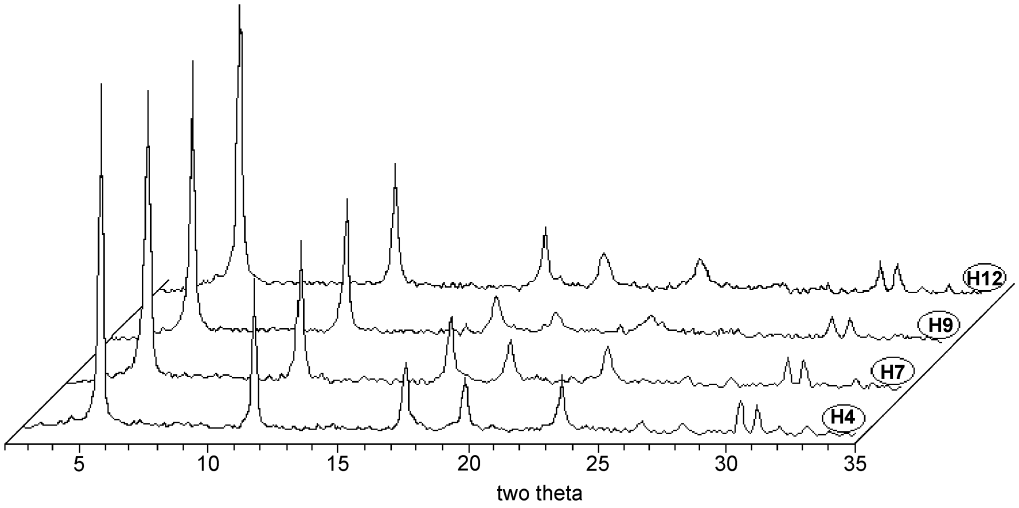


Fig. 3. XRD patterns for various LDHs.

Table 1
Main properties of LDH samples

Sample	Ni:Mg:Al (atomic ratio)		Adsorption heat of CO_2 at 353 K (J/g)	BET area (m^2/g)	Weight loss (%)
	Calc.	Meas.			
H4	0:2:1	2.01:1.0	42.08	31.3	42.98
H7	0.33:1.67:1	0.31:1.69:1.0	57.97	53.2	41.93
H9	1:1:1	0.96:1.04:1.0	47.33	63.4	37.36
H12	2:0:1	1.98:1.0	20.28	56.9	33.71

acetonitrile as solvent. The organic solvent forms a single phase with the substrate and hydrogen peroxide solution. The influence of the nature of the thioether, the type of the catalyst, temperature of the reaction and reaction time on the activity and selectivity in this reaction has been investigated.

3.2.1. *Effect of the nature of the thioether*

It is known that organic sulfides are oxidized by hydrogen peroxide in a heterolytic process involving the nucleophilic attack of the sulfur atom on the oxygen [9,10]. Generally, the reactivity of thioethers is correlated to the nucleophilicity of the sulfur atom, so that dialkylsulfide are more easily oxidized than diarylsulfide by electrophilic oxidant. Fig. 4 shows the thioether conversion versus time for the oxidation of propylsulfide (Pr_2S), methylphenylsulfide (MeSPh) and phenylsulfide (Ph_2S), over H9 and without catalyst.

These results lead to the following remarks:

- propylsulfide, an alkylsulfide, can be oxidized to some extent even without catalyst, but, under such conditions, phenylsulphide (an arylsulphide) is found to be unreactive;
- LDH catalyst shows a good activity in the oxidation reaction of all substrates;
- the thioethers are oxidized at different rates depending on the electron density of the sulfur atom $Pr_2S >$ MeSPh $> Ph_2S$.

It is interesting to point out that a similar order of the reactivity has been reported by Hulea et al. [3], in the case of the thioethers oxidation with H_2O_2 over Ti-containing zeolites.

The oxidation of thioethers can yield either the corresponding sulfoxide or sulfone, or both, depending on the reaction conditions. It is to be noted that under our conditions, both sulfoxide and sulfone are oxidation reaction products. Fig. 5 shows a typical profile for the evolution of oxidation reaction, where the sulfoxide and sulfone formation are consecutive steps (see Eq. (1)).

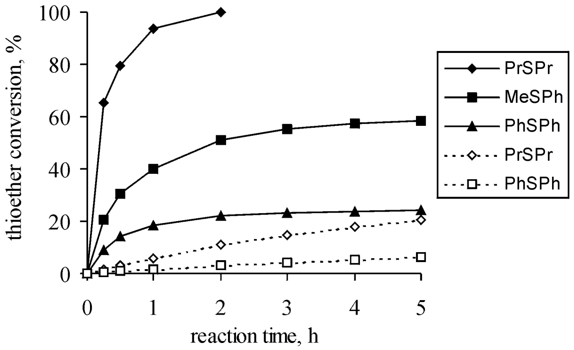


Fig. 4. Kinetics of sulfoxidation of different thioethers with H_2O_2 at 323 K in acetonitrile. $C_{\text{catal.}} = 4.54$ g/l; (—) H9 catalyst; (- - -) without catalyst.

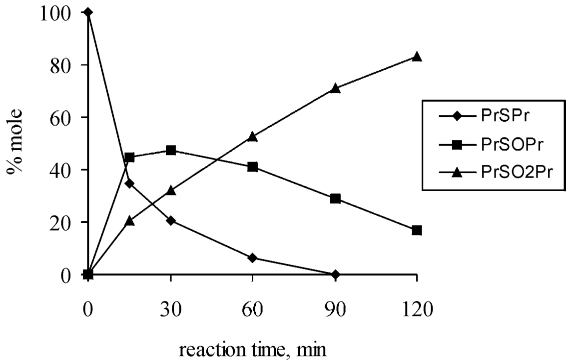


Fig. 5. Time progression of concentrations for propylsulfide oxidation with H_2O_2 over H9 catalyst, in acetonitrile, at 323 K.

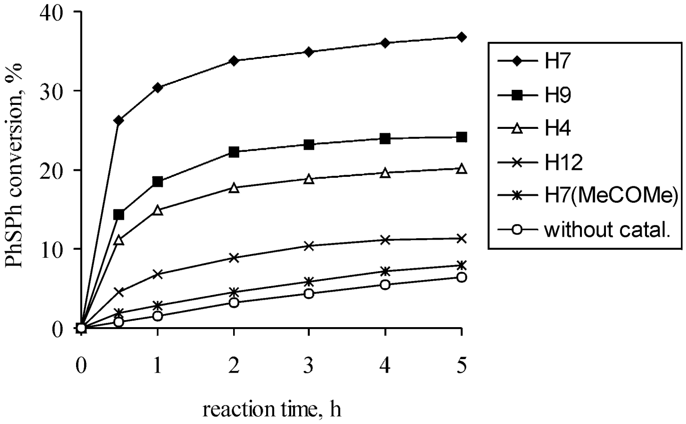


Fig. 6. Influence of the type of catalyst on the oxidation reaction of Ph_2S by H_2O_2 at 323 K; $C_{\mathrm{catal.}} = 4.54$ g/l.

3.2.2. *Effect of the nature of the catalyst*

The LDHs described above have been tested in the oxidation of phenylsulfide, chosen as model molecule. The oxidation of Ph_2S with H_2O_2 was carried out at 323 K in the presence of acetonitrile as solvent.

The results obtained show that Ph_2S conversion depends strongly on the nature of the catalyst, Fig. 6. Under similar conditions, the catalytic activity is in the following order:

$$H7 > H9 > H4 > H12$$

This order is similar to the one found for the heat of CO_2 adsorption (Table 1) measured for these catalysts. Therefore, it could be assumed that the catalytic activity depends on the basicity of catalysts, the catalytic activity increasing with the catalyst basicity.

Also, it can be observed from Fig. 6 that in the first stage the oxidation reaction occurs at a high rate, but later the reaction rate decreases. This behavior can be explained taking into account the decrease of the hydrogen peroxide concentration due to the parallel reaction of decomposition

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2}O_2$$

This reaction has been observed for all catalysts. It can be noted that the decomposition reaction occurs in the absence of the thioether, too.

If the oxidation reaction is carried out using acetone as solvent a low conversion of Ph_2S is obtained (Fig. 6). This result emphasizes the essential role of nitrile in the catalytic oxidation of thioethers by hydrogen peroxide. The oxidation of thioethers catalyzed by LDH occurs only in the presence of a nitrile compound.

3.2.3. *Influence of the reaction temperature*

The effect of the reaction temperature on the Ph_2S oxidation by H_2O_2 over H7 catalyst is shown in Fig. 7, where the conversion of organic sulfide versus time is plotted for the reactions carried out at 303, 323 and 343 K. From these results, it can be seen that temperature influences strongly the initial rate of Ph_2S

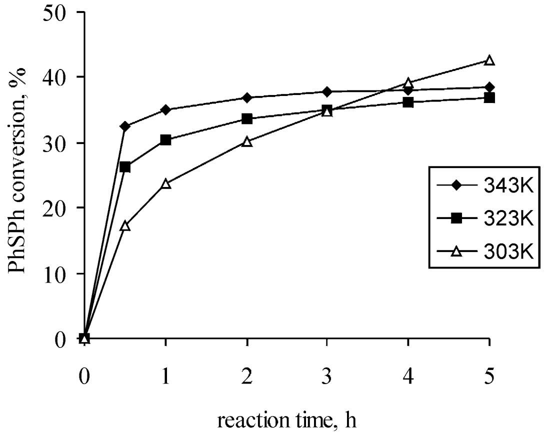
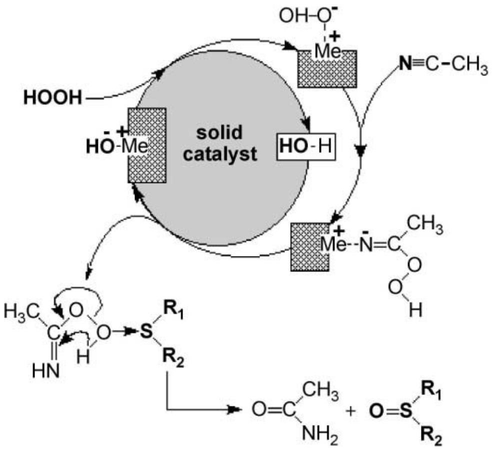


Fig. 7. Effect of the reaction temperature on the Ph_2S conversion in the oxidation reaction by H_2O_2 over H7; $C_{\mathrm{catal.}} = 4.54$ g/l; solvent: acetonitrile.



Scheme 2.

oxidation, when the hydrogen peroxide concentration is high.

As it was already mentioned, the hydrogen peroxide is also consumed in the parallel reaction of decomposition, which is favored by high temperatures. As a consequence, low temperatures are recommended (e.g. 303 K) if hydrogen peroxide has to be efficiently used.

3.2.4. The mechanism of the sulfoxidation reaction

The results presented above show that H_2O_2 alone, without any catalyst, is a poor oxidant for thioethers sulfoxidation (Fig. 4). The LDH materials are able to catalyze this reaction, and the catalytic activity depends strongly on the basicity of the solid (Fig. 6). Moreover, the oxidation hardly occurred in the presence of a solvent other than acetonitrile (Fig. 6).

It is known that the bases such as NaOH and KOH catalyze the epoxidation of olefins with H_2O_2in the presence of nitrile [11,12]. Recently, Ueno et al. [6] have shown that the LDH acts as an efficient base catalyst for the epoxidation reaction with hydrogen peroxide in the presence of benzonitrile and with methanol as solvent.

By analogy with the mechanism described in the literature for the alkene oxidation [11,12] and sulfoxidation of thioethers with H_2O_2 over Ti-containing zeolites [3], we propose the following mechanism for the thioethers sulfoxidation catalyzed by hydrotalcites (Scheme 2).

The active species in the oxidation reaction is the peroxyimidic acid arising from the addition of hydrogen peroxide to acetonitrile promoted by LDH as base catalyst. The catalytic function is exerted by hydroxyl groups on the LDH surface. In the second step, the oxygen atom is transferred from peroxyimic acid to sulfide by a nucleophilic attack of the sulfur atom to the peroxo group.

4. Conclusion

We have investigated the sulfoxidation reaction of thioethers with hydrogen peroxide over hydrotalcite as catalyst. The following remarks can be made as conclusion of this study:

- The LDHs are able to catalyze the sulfoxidation reaction of organic sulfide in the presence of a nitrile, under mild conditions, but the catalytic activity depends strongly on the basicity of the solid material.
- The sulfoxidation involves two steps: (a) the formation of peroxycarboximidic acid (PCIA) by the reaction of nitrile with H_2O_2 promoted by LDH as basic catalyst and (b) the oxygen transfer from PCIA to sulfide by a nucleophilic attack of the sulfur atom to the peroxo group. It can also be noted that the acetonitrile is converted into acetamide.
- A strong competition between the sulfoxidation reaction and the direct decomposition of hydrogen peroxide has been observed.

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