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Oxidation of Dibenzothiophene by Hydrogen Peroxide Catalyzed by Solid Bases

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The oxidation of dibenzothiophene by hydrogen peroxide was performed at 333 K using hydrotalcite and MgLa mixed oxide as catalysts and nitriles or methanol as solvents. High activity is found only after calcination followed by rehydration of hydrotalcite. The kinetics involves competitive adsorption of the reactants. Of the nitriles, acetonitrile is the best solvent, while much lower reaction rates are observed in methanol. Decomposition of hydrogen peroxide into oxygen is also observed for hydrotalcites and is the major reaction above 353 K. This reaction does not occur in the absence of nitrile and is faster over the MgLa mixed oxide of higher basic strength, in agreement with the decomposition of an iminoperacid intermediate formed by the base-catalyzed addition of hydrogen peroxide to the nitrile. The activity increases with increasing Mg/Al ratio due to a lower rate of H_2O_2 decomposition attributed to a lower basicity of the solid.

Key Words: **oxidative HDS assisted by nitriles; activation of hydrotalcite; basic catalysis; kinetics of oxidation; dibenzothiophene.**

INTRODUCTION

Environmental concerns are the driving force behind the goal of removing sulfur compounds from hydrocarbon-based distillate fuels, initially because of the tendency of the compounds to produce precursors to acid rain and airborne particulate material. The main reason for S removal is, however, that a few parts per million of sulfur are enough to poison the catalysts used for the purification of the exhaust gases of diesel cars (1). Several processes were proposed for solving the problem of removing these compounds from fuels. The most common industrial process is the treatment of the fuel with hydrogen at high temperature and high pressure. This hydrotreating process, hydrodesulfurization (HDS), is relatively expensive, especially for the fractions corresponding to diesel fuels, because these feeds contain the S compounds that are most refractory to HDS. Therefore, other processes were investigated for the same purpose, and recent research has focused on the oxidation of sulfur compounds, coupled with the extraction of the resulting sulfone by means of a solvent. Using peracetic acid at 356 K to treat a light atmospheric gas oil with an initial sulfur content of 0.42 wt%, Gore *et al.* reported 96% conversion of sulfur compounds after 1 h (2, 3). The process could be also applied using perboric, persulfuric, and peracetic acids or ozone. This oxidation procedure is very well suited to desulfuration, because the compounds, which react faster in oxidation, are substituted thiophenes, which show the lowest reactivity in HDS.

Peracids do not require a catalyst but are more expensive than hydrogen peroxide; a second possibility is to use H_2O_2 in the presence of a catalyst: methyltrioxorhenium(VII) (CH_3ReO_3) (4), CF_3COOH (5), formic acid (6), and recently titano silicates (7) were reported. While TS-1 was not very active due to the restricted access of reactants to the porosity, Ti-beta and Ti-HMS proved to be effective in the liquid phase, with Ti-beta reaching conversion above 90% after 5 h at 333 K. On a real kerosene charge, 90% removal of sulfur was observed after 2 h. Acetonitrile seems to be the best solvent for this reaction, but methanol and ethanol could also be used. When nitriles are used as solvents, hydrogen peroxide forms a peroxycarboximidic acid in the presence of a solid base such as hydrotalcite (HT). Indeed, HT acts as a catalyst to form a perhydroxyl anion species (HOO^-), which in turn nucleophilically attacks the nitrile to generate peroxycarboximidic acid, which is an active intermediate oxidant (8). The addition of hydrogen peroxide on nitriles was first performed in 1961 in organic chemistry (9), and the reaction mechanism depicted in Scheme 1 is widely accepted (10).

The peroxycarboximidic acid is too reactive to be isolated but its existence was proved by vibrational spectroscopy (11). It has been shown that step 1 is slow and that step 2, which leads to the decomposition of hydrogen peroxide, is fast. In the presence of an olefin, the iminoperacid reacts at the double bond to give dioxolane, which decomposes into the epoxide and the amide (8). With HTs, the best additives are benzonitrile and dicyanobenzene (12) and the same effect can be obtained by adding an amide (13). This reaction enables the epoxidation of a large spectrum of substrates but leads to the consumption of the nitrile or amide additive. Selective oxidation can be extended to epoxidation of

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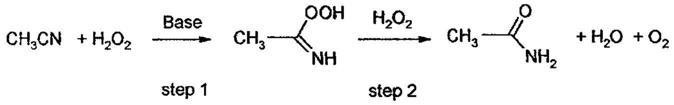

SCHEME 1. Formation and decomposition of peroxycarboximidic acid.

unfunctionalized olefins (14) and has recently been applied to the oxidation of thioethers to sulfones using calcined HTs (15). The evaluation of the possibilities of basic catalysis for oxidative desulfurization of benzothiophene derivatives and the comparison of the results with those of Ti-BEA were of interest. We report here the results obtained with different solid bases including HT and a La_2O_3/MgO mixed oxide of high basic strength.

EXPERIMENTAL

Preparation of the Catalyst Precursors

HTs were prepared by co-precipitation at 338 K and pH 9 according to experimental procedures described in detail elsewhere (16–19). Aqueous solutions containing the first 0.75 mol/L of $MgCl_2 \cdot 6H_2O$ and 0.25 mol/L of $AlCl_3 \cdot 6H_2O$ (for a Mg/Al ratio = 3) and the second 2 mol/L of KOH and 0.5 mol/L of K_2CO_3 were introduced by two electric pumps to a 4-L flask and mixed vigorously. The mixture was kept at 338 K for 18 h and was stirred continuously. The precipitate was washed several times until the solution was free of chloride ions ($AgNO_3$ test) and then dried at 393 K.

The products of synthesis contain Cl^- and CO_3^{2-} as charge-compensating anions. They were exchanged by carbonates using a solution of Na_2CO_3: 2 g of HT for 100 ml of a 0.2 M solution of Na_2CO_3 stirred at 343 K for 2 h. A MgLa mixed oxide with a Mg/La atomic ratio of 3 was obtained by co-precipitation of Mg and La nitrates at a constant pH of 10.

Activation of the Catalysts

Catalysts (about 0.15 g) were first heated to 723 K in a flow of nitrogen at 10 K/min, and were kept at this temperature for 12 h. In rehydration experiments, the HT was first decarbonated, cooled to room temperature, and treated in a flow of nitrogen saturated with the vapor pressure of water at this temperature. HT-13 (18) represents a sample of HT calcined at 723 K and treated for 18 h in a flow of nitrogen saturated by water. The MgLa mixed oxide was activated at 923 K and used without rehydration.

Characterizations

X-ray powder diffraction patterns were recorded on a Phillips instrument using Cu$K\alpha$ 1 radiation. The isotherm for N_2 adsorption at 77 K was determined on solids activated at 723 K in N_2 or air, then desorbed *in situ* at 473 K in vacuum. Thermal analysis of the solids was performed on a SETARAM apparatus, and the intensity of the mass 44 characteristic of CO_2 was measured during thermal analysis.

Catalytic Measurements

The oxidation of dibenzothiophene (DBT) and diethylsulfide by hydrogen peroxide was studied in a batch reactor composed of a triple-necked 50-mL round-bottomed flask, which was heated to 298–373 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 (30% in water, Prolabo) 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), freshly activated at 723 K and rehydrated at room temperature, 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. With acetonitrile as the solvent the conversion of DBT exclusively gave sulfones on HT, such that the conversion of DBT corresponds to the sulfone yield, defined as the ratio of moles of DBT converted to sulfone to moles of DBT introduced.

It was also observed that some of the H_2O_2 was decomposed into oxygen:

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2.$$

The material balance of the reaction was established by analysis of the products of oxidation and by volumetric measurement of the amount of oxygen evolved during the reaction. From this experimental measurement, the selectivity $S(O_2)$ of decomposition of H_2O_2 is expressed as a ratio of the number of moles of oxygen evolved to half the number of moles of H_2O_2 engaged in the reaction.

RESULTS AND DISCUSSION

Characterization of the Catalysts

Table 1 lists the chemical composition of the different solids. The characterization of HTs was reported elsewhere (20). The XRD patterns show that all HT samples are pure and of good crystallinity. The structure of the HTs exists in the range 1.5 < Mg/Al < 4.5 (17, 19); a sample with a Mg/Al ratio of 6 must contain an excess of amorphous MgO, which is undetectable by XRD. The calcination of HTs results in mesoporous mixed oxides with a high surface area, and it was reported that rehydration leads to a considerable loss of surface area. Rehydration restores the layered structure

TABLE 1

Chemical Compositions of the Hydrotalcites Used

Sample	Mg/Al solution	Mg/Al solid	Chemical composition
HT-6	2.02	1.82	$Mg_{0.64}Al_{0.36}(OH)_2(CO_3)_{0.17}(NO_3)_{0.0004}K_{0.0005}$, 1.2 H_2O
HT-13	2.99	2.93	$Mg_{0.75}Al_{0.25}(OH)_2(CO_3)_{0.15}(NO_3)_{0.0003}K_{0.0004}$, 0.47 H_2O
HT-14	4	3.90	$Mg_{0.8}Al_{0.2}(OH)_2(CO_3)_{0.18}(NO_3)_{0.0067}K_{<0.00002}$, 0.52 H_2O
HT-15	5	4.85	$Mg_{0.83}Al_{0.17}(OH)_2(CO_3)_{0.19}(NO_3)_{0.017}K_{<0.00003}$, 0.24 H_2O
HT-16	6	5.79	$Mg_{0.85}Al_{0.15}(OH)_2(CO_3)_{0.24}(NO_3)_{0.017}K_{<0.0003}$, 0.5 H_2O

and converts the solid to a low surface area (about 20 m^2/g) of meixnerite-like material with OH^- as the compensating anions (21).

XRD indicates that the MgLa mixed oxide is a biphasic system containing both magnesia and La carbonates (Fig. 1). The surface area of this mixed oxide is 45 m^2/g after calcination at 923 K. The solid probably consists of a layer of La oxide deposited on magnesia. The basic properties can be evaluated from the thermal desorption of CO_2 measured by mass spectrometry (Fig. 2) for two HTs and the MgLa sample. This analysis showed that MgLa is decarbonated at about 875 K and is a stronger base than either HT-13 or HT-15, which are decarbonated below 700 K. The intensity of the CO_2 peak, however, is much more intense on HT-13 than on HT-15, and shows a higher number of sites on HT-13.

Effect of the Activation Conditions

The effects of the activation conditions were investigated under the following conditions: 0.05 M substrate, 10 g/L catalyst, and 10 mol/mol hydrogen peroxide/substrate, 333 K reaction temperature (Fig. 3). Nondecarbonated HT and the mixed oxide obtained after heat treatment in nitrogen or air show low activity. Catalytic activity increased when the sample was first decarbonated and then rehydrated. When the rehydration time is short, activation occurs during the course of the reaction. Constant activity is observed after about 10 h of rehydration, and the standard rehydration time was 18 h. With MgLa-3 as the catalyst oxidized sulfur compounds were not observed and the only reaction product was oxygen produced from hydrogen peroxide with a selectivity close to 90–100%. During pretreatment the solids undergo decarbonation and dehydroxylation; the low activity of the calcined oxides suggests that basic hydroxyls are required for the oxidation reaction.

Influence of the Reaction Conditions

The catalyst used in this study was HT-13 (Mg/Al ratio = 2.9), rehydrated for 18 h, with a small surface area and no microporosity (21). As reported earlier the reaction yields the sulfone and oxygen only. Small amounts of acetamide were detected (Scheme 1).

The influence of hydrogen peroxide and DBT concentrations on the initial rate of the reaction is shown in Figs. 4 and 5. The reaction is initially first-order, and the rate goes through a maximum as a function of the concentration of DBT, suggesting competition between the two reactants

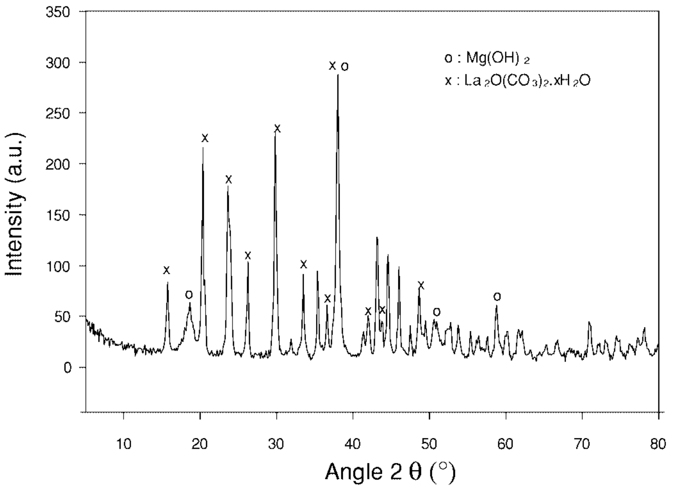

FIG. 1. Powder XRD pattern of MgLa = 3 mixed oxide.

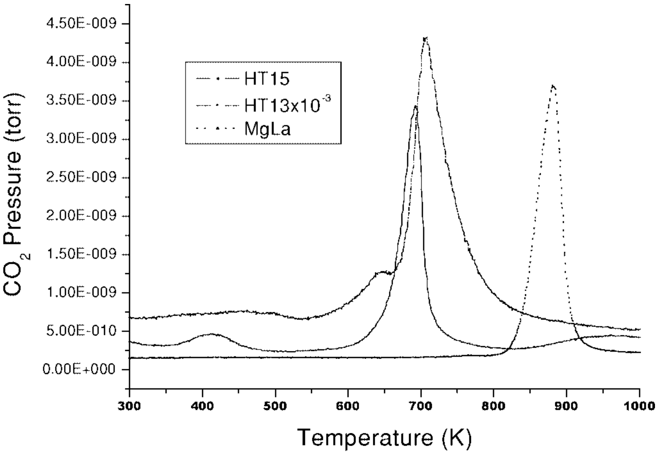

FIG. 2. Variations in the intensity of the mass 44 peak, normalized to 1 g of sample, as a function of temperature for MgLa-3 mixed oxide and two HTs.

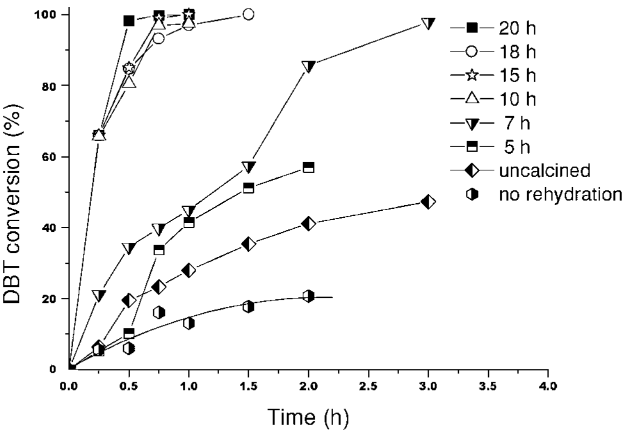

FIG. 3. Effect of time of rehydration on catalytic activity at 333 K of HT-13 calcined at 723 K.

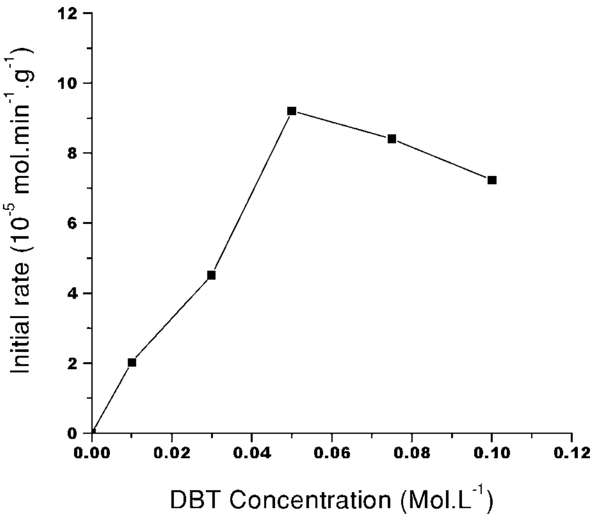

FIG. 4. Effect of DBT concentration on the rate of HT-13, at 333 K and a constant concentration of hydrogen peroxide (0.25 M).

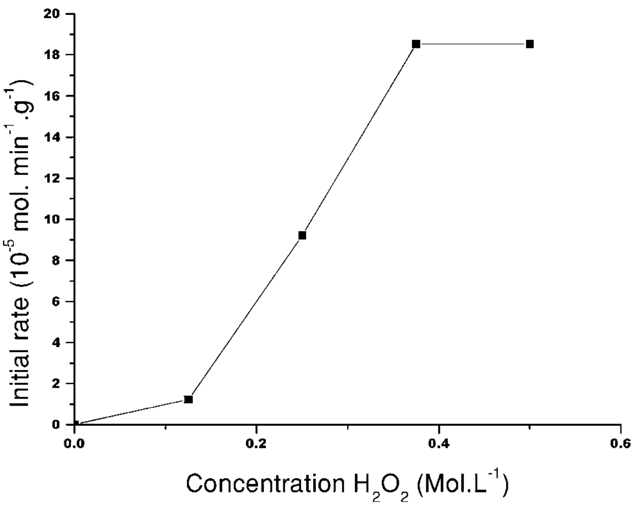

FIG. 5. Effect of concentration of hydrogen peroxide on the initial rate of HT-13 at 333 K and a constant concentration of DBT (0.05 M).

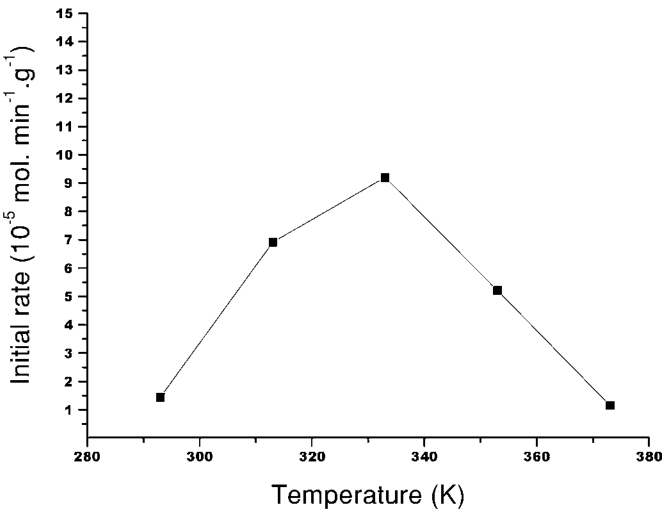

FIG. 6. Effect of reaction temperature on the initial rate of DBT oxidation on HT-13.

for adsorption. Fig. 6 shows the effect of the reaction temperature on the initial rate, measured with a mixture of DBT/H_2O_2 (0.5/2.5). The initial rate reaches a maximum at about 333 K. The selectivity for the decomposition of hydrogen peroxide to oxygen increased with the reaction temperature (Table 2). At the higher temperatures, the rate of decomposition of hydrogen peroxide was fast and affected the initial rate.

The decomposition of hydrogen peroxide was relatively slow on the uncalcined sample, higher on the mixed oxides, and decreased after rehydration. The LaMg mixed oxide showed selectivity to O_2 above 90%. The faster decomposition on a base as strong as LaMg and calcined HT (Table 2) is in agreement with the basic mechanism represented by Scheme 1.

TABLE 2

Selectivity of Formation of Oxygen after 90-min Reactions at Different Temperatures Using 0.5 mmol DBT

Catalyst	Reaction temperature (K)	Oxygen selectivity (%)
HT-13 as synthesized	333	17
HT-13 calcined	333	53 88[a]
HT-13 (18)	298	30
HT-13 (18)	313	47
HT-6 (18)	333	73
HT-14 (18)	333	67
HT-15 (18)	333	50
HT-16 (18)	333	40
HT-13 (18)	353	53
HT-13 (18)	373	97

[a] After 3 h.

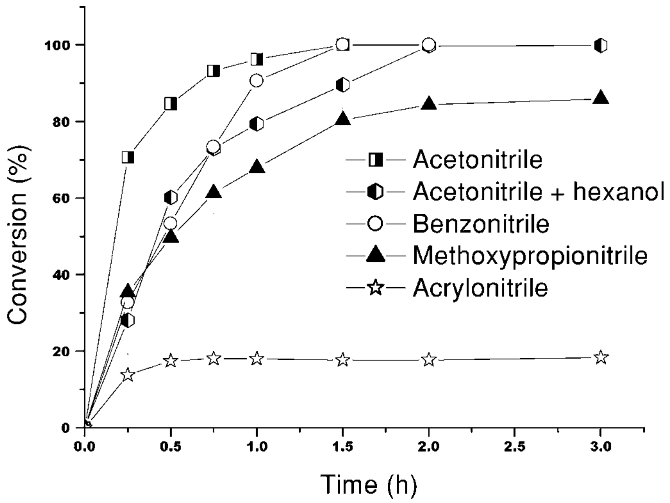

FIG. 7. Effect of the nature of the solvent on the oxidation of DBT at 333 K.

The effects of the solvent were investigated by comparing methanol, acetonitrile, benzonitrile, acrylonitrile (ACN), and 3-methoxypropionitrile (3MPN). The results are reported in Fig. 7 and Table 3. No reaction was observed with methanol as the solvent, even after partial rehydration for 3 h. Small amounts of 1-hexanol (1 mmol/10 mL of solvent in acetonitrile as the solvent) also had a detrimental effect. Since the mechanism involves the formation of perhydroxyl anions from hydrogen peroxide, competition between the alcohol and the hydrogen peroxide for adsorption at the surface can account for this inhibition. A comparison of the different nitriles shows that acetonitrile, benzonitrile, or 3-methoxypropionitrile give high final yields, with a higher reaction rate with acetonitrile. Dumitriu *et al.* (15) reported that the decomposition of H_2O_2 occurred in acetonitrile in the absence of thioether. Moreover, the decomposition of H_2O_2 was not observed during 3-cyclohexen-1-one epoxidation performed on HT in toluene as the solvent (22). O_2 formation must then be related to the specific chemical properties of acetonitrile, and step 2 of Scheme 1 is a well-established path for this reaction. Since step 1 is slow, the reactivity of the nitrile and the basic properties of the solid would then control O_2 formation.

TABLE 3

Influence of the Solvent on the Conversion of DBT on HT-13 at 333 K with H_2O_2/substrate ratio = 10

Catalyst	React time (h)	Solvent	Sulfone selectivity	DBT conv. (%)	O_2 selectivity (%)
HT-13 uncalcined	3	CH_3CN	100	47.3	17
HT-13 calcined	3	CH_3CN	100	32	53
HT-13 calcined[a]	6	CH_3OH	0	0	
HT-13 (18)	1.5	CH_3CN	100	96	33
HT-13 (18)	3	C_6H_5CN	100	100	20
HT-13 (18)	3	3MPN	100	86	18
HT-13 (18)	3	ACN		17.6	22

[a] H_2O_2/substrate ratio = 5.

Effect of the Basicity of the Catalyst

The basic properties of MgAl HT change when the Mg/Al ratio and the heat treatments are changed. The uncalcined HT-13 sample showed low activity for oxidation of DBT (Fig. 3), suggesting that basicity is involved in the reaction. The rate of isomerization of isophorone enables the determination of the number of basic sites of HT in the liquid phase after rehydration, in conditions close to those of the reaction. The effects of the Mg/Al ratio on the rates of DBT oxidation, the final yield in sulfone, and rate of isophorone isomerization are given in Fig. 8. At a ratio Mg/Al of about 3, isophorone isomerization shows maximum activity as observed for many other reactions such as Knoevenagel condensation (23, 24) or aldolization (25). In contrast, HT oxidation activity increases steadily with the Mg content up to Mg/Al = 6. The samples with Mg/Al ratios higher than 5 are not single phases, and HT-16 (Mg/Al ratio = 5.7) is probably composed of a surface layer of amorphous magnesia supported on HT, and probably shows the basic properties of magnesia. Modification of catalyst composition affects the final yield to a greater extent than the initial rate; this is attributed to a lower selectivity for H_2O_2 decomposition at high Mg/Al ratios.

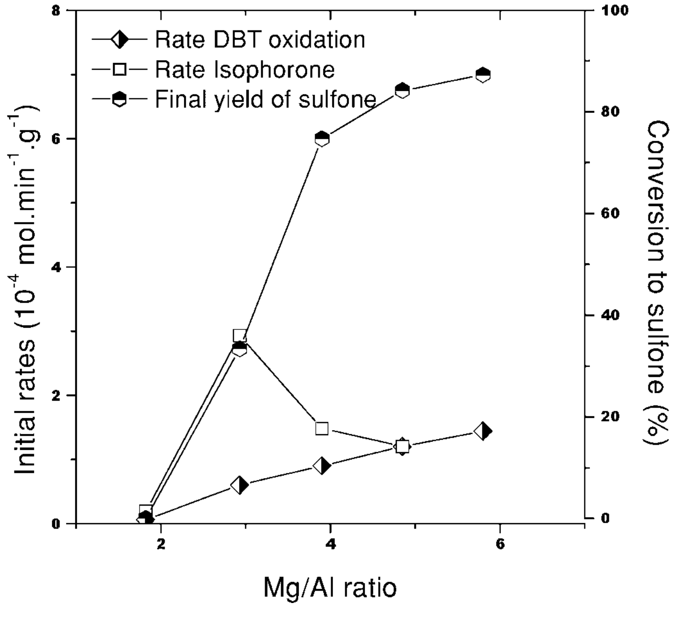

FIG. 8. Initial rates of oxidation and conversion after 90 min of DBT compared to the rate of isomerization of isophorone on HTs of different Al contents, which were calcined and then rehydrated for 18 h.

Comparison of Ti-Catalysts with Hydrotalcites

The comparison can be made using the results reported by Hulea *et al.* (7) at 333 K for Ti-BEA in acetonitrile as the solvent; the DBT concentration was 0.0645 M, catalyst concentration was 3.22 g/L, and H_2O_2/DBT was equal to 2.4 mol/mol. Since conversion reached 34% in 120 min, the rate was 5.6×10^{-5} mol min^{-1} g^{-1} for Ti-BEA. For HT, the first point (Fig. 5) was measured at 333 K in acetonitrile solvent; the substrate concentration was 0.05 M, catalyst concentration 10 g/L, and H_2O_2/DBT was equal to 2.5 mol/mol. The rate was 1.2×10^{-5} mol min^{-1} g^{-1}. The real difference is smaller, because hydrotalcite loses about 50% weight upon calcination. The specific activity per square meter would favor HT (surface area 20 m^2/g) compared to Ti-BEA (470 m^2/g).

In conclusion, the oxidation of DBT to sulfone is possible by a base-catalyzed mechanism on HT, using a solid that was calcined and then rehydrated, suggesting that the catalytic sites are probably hydroxyls. The best solvent is acetonitrile, which facilitates the possibility that peroxycarboximidic acid is an intermediate. The activity reached by this process is comparable to that obtained with Ti catalysts.

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