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Catalyst screening for oxidative desulfurization using hydrogen peroxide

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Abstract

Oxidation of a mixture of thiophene, benzothiophene and dibenzothiophene with hydrogen peroxide using supported Pd, Cr_2O_3, unsupported manganese oxides and a commercial Co-Mo/Al_2O_3 as catalysts has been studied in a mixture of hexadecane and acetonitrile. Based solely on the conversion of each organic sulfur compound, the ranking of catalyst efficiency found was: supported Pd > Cr_2O_3 ≈ manganese oxides ≈ Co-Mo/Al_2O_3. The influence of the calcination temperature on synthesized manganese oxides was also investigated. Mn_3O_4, amorphous manganese compounds, Mn_2O_3 and MnO_2 showed a similar catalytic activity independent of the hydrogen peroxide concentration. According to these preliminary results, it seemed that the catalyzed decomposition of the hydrogen peroxide competes with the oxidative desulfurization, however, at short reaction time (10 min) conversions at around 60–70% of thiophene were reached.

Keywords: Oxidative desulfurization; Hydrogen peroxide; Mn oxides catalysts

1. Introduction

New processes capable of a higher desulfurization efficiency to produce ultra-low sulfur fuels are being developed [1]. In particular, the oxidative desulfurization process (ODP) appears very promising and is currently receiving growing attention [2–10]. ODP can be carried out under very mild conditions (room temperature and atmospheric pressure) compared with the more severe conditions used in the conventional catalytic hydrodesulfurization (HDS). The ODP is based on the well-known propensity of organic sulfur compounds to be oxidized. It consists of an oxidation reaction followed by the extraction of the oxidized products. The physicochemical properties of sulfones are significantly different from those of hydrocarbon in fuel oil and they can be easily removed by distillation, solvent extraction, adsorption or decomposition [4,7,11]. Many types of oxidants have been used [5]. However, hydrogen peroxide is considered the most promising oxidation agent in terms of selectivity, product quality, safety, environmental impact and process economics [7].

One of the main advantages of the ODP is that the most refractory sulfur compounds (e.g. alkylated dibenzothiophenes) show a higher reactivity than that of HDS in which expensive hydrogen is used. The reactivities of the compounds seem to correlate well with their electronic density except with the 4,6 dimetyl dibenzothiophene [3]. The oxidation of sulfides to sulfones is generally carried out by reaction with a peroxycarboxylic acid generated in situ by hydrogen peroxide and the appropriate carboxylic acid [5].

The aim of the present work was to test the activity of solids well recognized as oxidation catalysts but focusing on the inexpensive manganese oxides which are considered to be the most effective catalysts for the hydrogen peroxide decomposition [12], Mn_2O_3, Mn_3O_4, MnO_2 and mixtures were prepared, characterized and tested in the oxidative desulfurization of model organic sulfur compounds.

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2. Experimental

All chemicals were commercial products, used as supplied. The palladium catalysts (1 wt.%) were prepared by impregnating the Al_2O_3, MgO-Al_2O_3, and ZrO_2 with an aqueous solution of $PdCl_2{\cdot}2H_2O$ [13,14]. The Pd-supported catalysts were dried at 110 °C and then calcined at 400 °C. Before the testing, all the catalysts were reduced in hydrogen flow at 500 °C. The $Cr_2O_3/ZnAl_2O_4$ catalyst was prepared by impregnation of zinc aluminate [15] with an alcoholic solution of Cr nitrate (III). After eliminating the excess of solvent, the catalyst was calcined at 600 °C. The final amount of Cr_2O_3 was 7 wt.%. Manganese oxides were prepared by precipitation at room temperature using an aqueous solution of manganese nitrate (II) and ammonium hydroxide as precipitant agent [16]. The preparation was carried out in several steps. Initially the reactor was maintained at pH constant (11) in air flow, then, the cobalt solution was added slowly and the final pH was 7.9. Secondly, the sample was irradiated in a domestic oven (Philco, 90 W, 2.45 MHz) for 1 min (crystallization step). The precipitation thus obtained was washed with distilled water, centrifuged and dried at vacuum and room temperature. The precursor was calcined in air flow (40 mL/min) with a rate of 10 °C/min to 100, 300, 500, 700 and 950 °C. The reference compound was MnO_2 (Baker).

The XRD patterns were obtained in a Siemens D-500 coupled to a Cu anode. The catalysts were evaluated in the oxidative desulphurization reaction using a glass reactor operated in batch and with a recirculation bath to control the temperature. A mixture of thiophene, benzothiophene and dibenzothiophene, containing 3000 ppm of the first and second ones and 2000 ppm of the third one, were dissolved in hexadecane. Hydrogen peroxide (30 vol.%) was the reducing agent and the solvent was acetonitrile to perform the extraction of the oxidation products. The reaction mixture was added in a proportion of 1:1 and simultaneously added with the oxidizing agent. Previously, the mixture was vigorously stirred at constant temperature of 60 °C. Finally, the catalyst was added to the reactor. The reaction time was 50 min, with sampling each 5 min. The analysis of the reactor effluent was carried out in a HPLC Waters using a Envirosep PP of Phenomenex of 125 mm × 4.5 mm, with a mobile phase of acetonitrile/water (60/40, v/v). A commercial HDS catalyst (Co-Mo/Al_2O_3) was a reference in the catalytic activity tests.

3. Results and discussion

The five supported Co-Mo, Cr_2O_3 and Pd catalysts as well as the unsupported Mn_3O_4 were tested in the oxidation of sulfur organic compounds by hydrogen peroxide. The experiments, performed at 60 °C (Fig. 1) reveal that roughly the same conversion for $Cr_2O_3/ZnAl_2O_4$ and Mn_3O_4, but the Co-Mo presented a slightly higher conversion in the case of benzothiophene and dibenziothiophene. However, the Pd catalysts sustain the most pronounced differences compared with the reference catalyst (Co-Mo). In particular, the Pd/MgO-Al_2O_3 catalyst showed a conversion of 85, 81 and 78% for thiophene, benzothiofene and dibenzothiophene, respectively, and the reference catalyst had 67, 59 and 54% in the same order. Pd/Al_2O_3 and Pd/ZrO_2 presented a similar conversion for the three sulfur organic compounds.

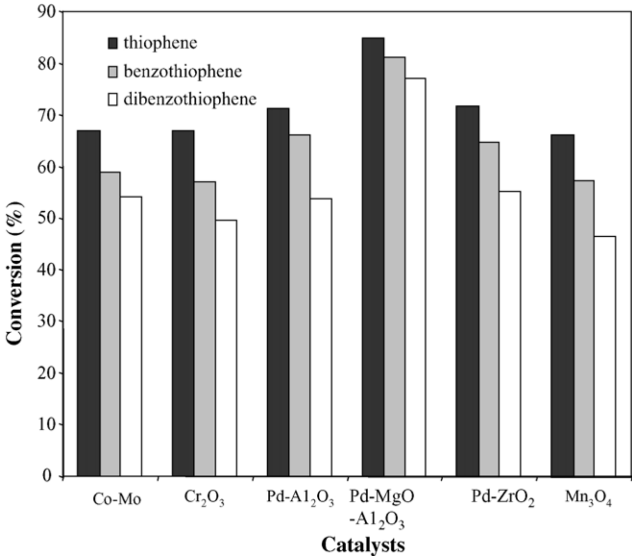

Fig. 1. Oxidation of thiophene (3000 ppm), benzothiophene (3000 ppm) and dibenzothiophene (2000 ppm) on the selected catalysts. Reaction conditions: temperature, 60 °C; reaction time, 20 min.

Fig. 2 presents the XRD patterns of Mn_3O_4 as a precursor of manganese oxide in the calcinations temperature range of 100, 300, 500, 700 and 950 °C. During the calcination step, the original microcrystalline Mn_3O_4 (Fig. 2a) was converted to an amorphous mixture of Mn compounds at 300 and 500 °C (Fig. 2b and c, respectively). However, a crystalline Mn_2O_3 and a small amount of MnO was obtained at 700 °C (Fig. 2d). At higher calcination temperature, 950 °C (Fig. 2e) practically all Mn_2O_3 was transformed to

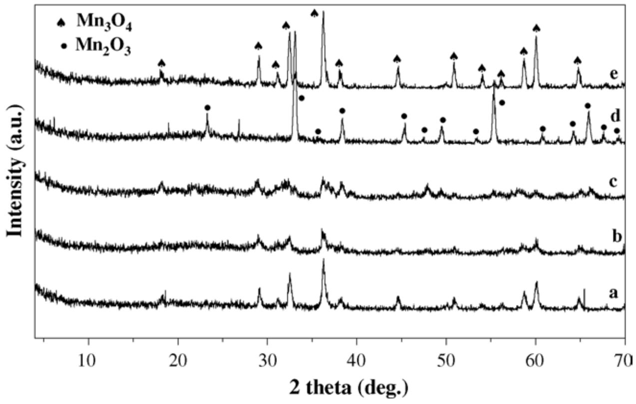

Fig. 2. X-ray diffraction patterns of manganese oxides calcined at different temperatures: (a) 100 °C; (b) 300 °C; (c) 500 °C; (d) 700 °C; (e) 950 °C.

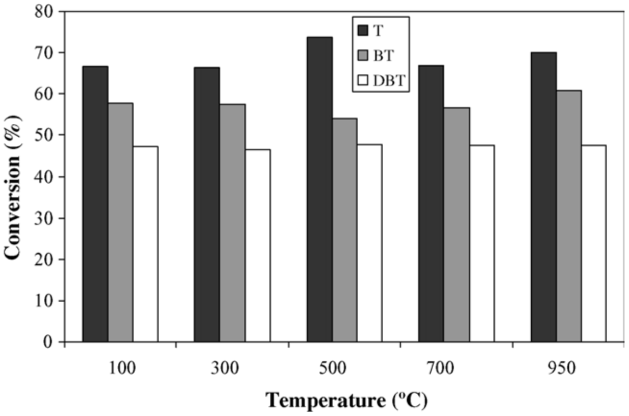

Fig. 3. Effect of calcination temperature of manganese oxides on the oxidation of thiophene (3000 ppm), benzothiophene (3000 ppm) and dibenzothiophene (2000 ppm). Reaction conditions: temperature, 60 °C; reaction time, 20 min.

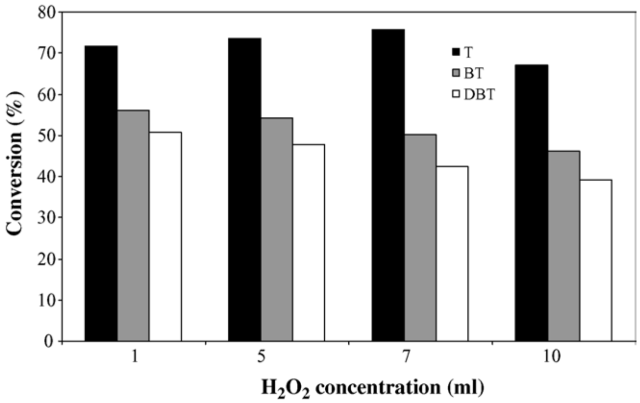

Fig. 4. Effect of H_2O_2 concentration on the oxidation of thiophene (3000 ppm), benzotiophene (3000 ppm) and dibenzothiophene (2000 ppm). Reaction conditions: temperature, 60 °C; reaction time, 20 min.

Mn_3O_4. This transformation could occur by the following reaction:

$$Mn_3O_4 \xrightarrow{700\,^{\circ}C} Mn_2O_3 + MnO \xrightarrow{950\,^{\circ}C} Mn_3O_4 \quad (1)$$

Fig. 3 shows the conversion of the mixture as a function of calcination temperature of the catalysts. A blank experiment was carried out without catalyst in order to check the effect of the homogeneous reaction and no conversion was detected. This means that the reaction proceeds by a catalytic species formed during the interaction of hydrogen peroxide with the manganese oxides. After 10 min of reaction, the conversion of the sulfur compounds, yielding only sulfones, did not change and was maintained constant until 40 min.

Although the amount of produced oxygen, during the non-productive decomposition of hydrogen peroxide, was not measured it was clear that this fast reaction was favored with respect to the oxidative desulfurization. In general terms, as can be seen in Fig. 3, the conversion of the organic sulfur compounds did not depend on the type of manganese oxide obtained after calcining in the range of 100–950 °C.

In Fig. 4, the conversion of sulfur compounds is presented at several concentrations of H_2O_2 using the sample calcined at 500 °C. It was observed that a small increase of conversion occurred as the H_2O_2 concentration was increased. However, with 10 mL of H_2O_2 added to the reaction mixture, the conversion decreased. These results suggest that the rate of hydrogen peroxide decomposition is proportional to the concentration of the catalytic complex formed between the manganese oxides and H_2O_2 [11].

4. Conclusion

A screening of several catalysts showed that supported Pd catalysts provided an oxidative desulfurization activity that was higher than that of Cr_2O_3/Al_2O_3 or Co-Mo/Al_2O_3 or unsupported Mn oxides. High temperature calcination (110–950 °C) of manganese oxides did not have an effect on the catalytic activity. An increase of H_2O_2 concentration from 1 to 7 mL in the reaction mixture favored the conversion of the sulfur compounds. The reaction could be explained by the fast decomposition of H_2O_2 forming a catalytic complex, which is able to activate the sulfur compounds into sulfones.

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