

## Solvent effect in heterogeneous oxidative reactions between dibenzothiophene and hydrogen peroxide

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### Introduction

The oxidation-extraction scheme to remove sulfur compounds is an attractive alternative to obtain diesel with ultra low sulfur content [1-2]. Acetonitrile (MeCN) and alcohols like methanol (MeOH) or ethanol (EtOH) have been tested on the heterogeneous oxidation of dibenzothiophene (DBT) by Figueras et al. [3] and Hulea et al. [4]. Although the authors have showed that DBT conversion varied depending of the solvent, its role has not been fully understood. Moreover, some mechanistic aspects involved in the extraction-reaction process occurring during the oxidative desulfurization of DBT are not clear. Thus, attention should be paid to establish a relation between the extraction capacity of solvents, their thermophysical properties and kinetic data. According with these aspects, experiments were carried out in order to study the effect of solvent when interacts with the oxidizing agent and catalyst in the oxidative reaction of DBT and hydrogen peroxide.

### Materials and Methods

A WO<sub>x</sub>-ZrO<sub>2</sub> sample was prepared by wet impregnation of zirconium oxyhydroxide with ammonium metatungstate at pH=10 (W loading = 20 wt.%) and calcined at 1073 K. The catalyst was characterized by XRD, N<sub>2</sub> physisorption and Raman spectroscopy before and after catalytic reaction. MeOH, EtOH, MeCN and  $\gamma$ -butyrolactone (GBL) were used as extraction solvents, while the oxidation was carried out with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). The reactions were performed in a Robinson-Mahoney glass batch reactor. DBT and dibenzothiophene sulfone (DBTO<sub>2</sub>) concentration in polar and non-polar phases were analyzed by gas chromatography.

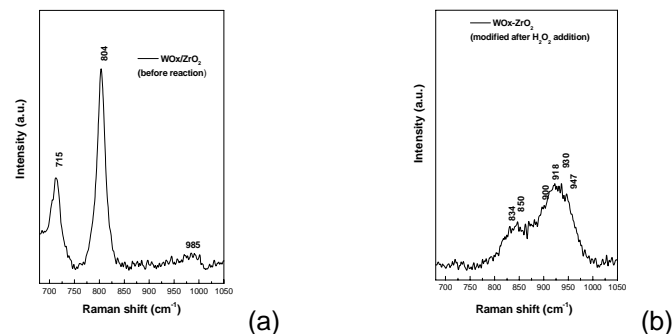
### Results and Discussion

The order of extraction capacity of solvents to remove DBT from n-hexadecane (n-C<sub>16</sub>) was GBL>MeCN>EtOH>MeOH. The transformation of DBT to DBTO<sub>2</sub> with MeCN or GBL was higher with respect to MeOH or EtOH. It can be proposed that the non-protic or aprotic character of the solvents could play an important role on the oxidation reactions, due to the fact that strong oxidant species (hydroxide HO<sup>-</sup> and perhydroxyl HO<sub>2</sub><sup>-</sup> ions) are formed by dissociation of H<sub>2</sub>O<sub>2</sub> or H<sub>2</sub>O only in aprotic solvents.

For the experiments in the presence of the catalyst, an increase on the DBT conversion of 1.6-1.7 times was observed as compared with the results from experiments without catalyst. Table 1 summarizes the rate constant (*k*) values at 333 K for the oxidation of DBT with H<sub>2</sub>O<sub>2</sub>. The reactivity with GBL is 1.5, 4.7 and 10.0 times higher than MeCN, EtOH and MeOH, respectively. This behaviour might be related to the hydrophilic and acidic

character of WO<sub>x</sub>-ZrO<sub>2</sub> catalyst. MeOH and EtOH molecules could be strongly adsorbed by WO<sub>x</sub>-ZrO<sub>2</sub> through hydroxyl groups of alcohols.

From characterization results, the contribution of the catalyst to the oxidation-extraction will be discussed. It can be proposed that the formation of surface peroxo-metal intermediates (W-O-O-H) may intervene in the oxidation reaction. These intermediates have been identified by Raman spectroscopy. After the oxidation reaction, three new shoulder bands at 900, 912 and 947 cm<sup>-1</sup> were formed, that could be assigned to  $\nu_{(W-O-Zr)}$ ,  $\nu_{(W-O-W)}$  and  $\nu_{(W=O)}$  modes, respectively. A discussion based on a proposal for the reaction-extraction mechanism will be presented considering evidences obtained from catalyst characterization.



**Figure 1.** Raman spectra for the WO<sub>x</sub>/ZrO<sub>2</sub> system (at 20 wt. % W, calcined at 1073 K in air for 3h). (a) WO<sub>x</sub>/ZrO<sub>2</sub> spectra before reaction and (b) after reaction.

**Table 1.** Effect of solvent on transformation of DBT to DBTO<sub>2</sub> at 333 K. Pseudo-first order rate constants (*k*) were calculated.

Solvent	$k \times 10^2$ (mol/g cat·min)
MeOH	0.36
EtOH	0.77
MeCN	2.32
GBL	3.60

### Significance

The understanding of the key aspects for the mechanism of the heterogeneous oxidation of dibenzothiophene is relevant to improve industrial processes to obtain low sulfur diesel.

### References

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