Chemoselective oxidation of 2-thiomethyl-4,6-dimethyl-pyrimidine, 2-thiobenzyl -4,6-dimethyl-pyrimidine and methyl-dodecylthioether over Ti-SBA-15 catalysts

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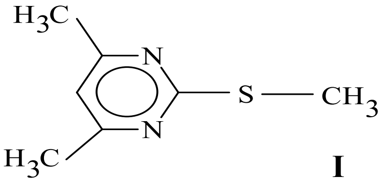
Introduction

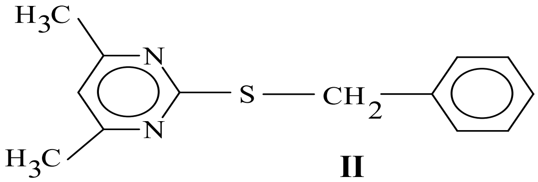
Chemoselective oxidation of organic sulfides to sulfoxides and sulfones is one of the very attractive catalytic oxidations because valuable synthons and pharmaceutical active compounds can be obtained in this way. Most of the reported syntheses were done in homogeneous conditions using titanium alkoxides as catalysts [1]. Heterogeneous catalysts have scarcely been reported in this reaction. Reddy et al. [2] showed that titanium containing molecular sieves may lead to a certain chemo- and stereoselectivity. Other type of titania-silica catalysts like titano-silicalites, mixed or sol-gel mixed oxides have also been used. [3]. Asymmetrization of titanium-containing heterogeneous catalysts is still doubtful. Our previous studies indicated that a stereoselective behavior of titanium-based catalysts might serve as an evidence of a titanium leaching [4].

The aim of this paper is to present results on selective oxidation of two pyrimidine-derivatized sulfides (**I** and **II**) and of methyl-dodecyl-thioether using Ti-SBA-15 catalysts. Separate oxidations using previously modified catalysts with chiral ligands like L(+)-tartaric acid or R(-)-α-metoxyphenylacetic acid, or by direct addition of these ligands in the reaction mixtures, have also been performed. The corresponding pyrimidine-derivatized sulfoxides are precious intermediates in the synthesis of agrochemical fungicides, pesticides and acaricides.



I

2-thiomethyl-4,6-dimethyl-pyrimidine



II

2-thiobenzyl-4,6-dimethyl-pyrimidine

Ti-SBA-15 catalysts with different Ti/Si ratios (1 to 2) and texture properties (610 to 980 m^2 g^{-1}, and pore size between 3.6 nm and 5.6 nm) were prepared. The catalysts were characterized using several tools: adsorption-desorption isotherms of N_2 at 77K, XRD, DRUV-Vis, FTIR and XPS. The catalytic tests were carried out in a glass-flask. Standard experiments used 10 mg catalyst and 100 mg sulfide under inert atmosphere. The reactions were carried out at room temperature for a sulfide:H_2O_2 ratio of 1:3.7, and reaction times between 10min and 5h. Dioxane, methanol and $CHCl_3$ were used as solvent. The analysis of the products was done by ^1H and ^{13}C

NMR operating at 300 MHz for ^1H and 75 MHz for ^{13}C. The optical purity of produced sulfoxide was checked by ^1H NMR using the Pirkle's reagent.

Results and Discussion

The oxidation of the pyrimidine derivatives and methyl-dodecyl-ether was total after 2.5 h. The selectivity to the corresponding sulfoxides is presented in Figs. 1 and 2. This was different for the two kinds of molecules as a function of the texture and titanium dispersion and loading. The increase of the surface area is accompanied by a decrease of the pore size that made titanium less accessible to large molecules as pyrimidine derivatives, but still accessible to methyl-dodecyl-ether. The catalyst with 920 $m^2\ g^{-1}$ behave differently, showing a mouth pore effect. Agglomeration of titanium (2% Ti) has also a negative effect. In the absence of the catalysts the conversion reached about 7% after 5h with a 100% selectivity to sulfone. These data clearly evidenced the contribution of the catalysts, indicating that the chemoselective oxidation of the thioether is a heterogeneous catalytic mediated reaction.

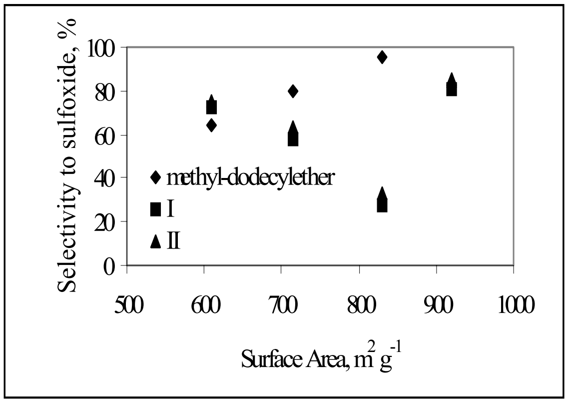


Fig. 1. Selectivity to sulfoxideas a function of surface area of Ti-SBA-15 catalysts (298 K; conversion 100%)

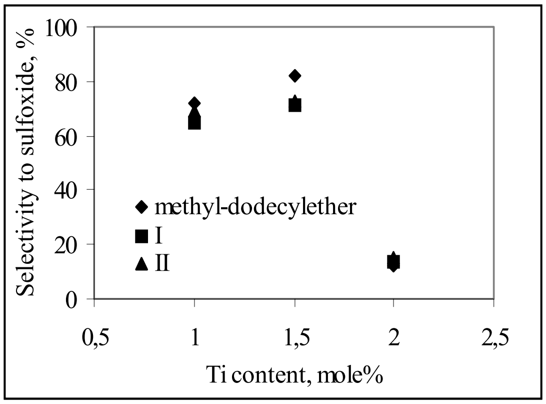


Fig. 2. Selectivity to sulfoxideas a function of titanium content (298 K; conversion 100%)

The modification of the catalysts with tartaric acid caused no changes in the catalysts activity, the conversion being also complete after 2.5 h. The modification with tartaric acid determined however important changes in the chemoselectivity. Except for the sample with a surface area of 920 $m^2\ g^{-1}$, the selectivity was increased. No e.e. was measured. The characterization of the catalysts as fresh and tested ones, and the analysis of the separated liquors after an other 4h reaction clearly indicated no leaching of titanium in these catalysts. In conclusion, heterogeneous oxidation of thioethers on Ti-SBA-15 catalysts led to chemoselective synthesis of sulfoxides.

References

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