



**LARGE MESOPOROUS ALUMINA SUPPORTED ALKALINE FLUORIDES –
EXCELLENT CATALYSTS FOR PRODUCTION OF BIODIESEL VIA
TRANSESTERIFICATION OF VEGETABLE OILS**

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Introduction

The valorification of biomass with the aim to obtain biofuels already entered in the common philosophy and found industrial applications. These refer to the transesterification of vegetable oils with methanol in the presence of homogeneous basic catalysts. However, from both the green and the environmental point of view replacing the homogeneous catalysts with heterogeneous stable systems represents an important target. In this study we provide evidences about the catalytic performances of a heterogeneous system that might be prepared and manipulated in a very simple mode. Evidences about the nature of the active site in these catalysts are provided as well.

Results and discussions

KF and Cs/Al₂O₃ catalysts with different loadings from 1 till 20 wt% were prepared by wetness impregnation of basic mesoporous alumina synthesized according to literature data [1,2]. Activation of the catalysts was carried out in nitrogen and followed by *in situ* XRD measurements. The increase of the temperature over 250 °C corresponded to the diminution of the intensity of the reflexion planes of the AlO(OH) phase and to the formation of K₃AlF₆ or Cs₃AlF₆ phases, respectively. At 500 °C this process is completed. This process was also confirmed by ²⁷Al MAS NMR for samples calcined at different temperatures, and by in-situ DR-UV-Vis measurements. From the interaction of the alkaline fluorides with the support it is also resulting MOH, which remains strongly chemisorbed onto the alumina surface. DRIFTS investigation of the catalysts using NH₃ and CD₃Cl confirmed the presence of the basic sites. Furthermore, calcination in air is



leading to the formation of carbonate species that can be hardly removed. XPS and textural analysis completed the characterization of the catalysts.

Transesterification of different vegetable oils (sunflower, soybean, rapeseed) was carried out using three different experimental procedures, ie autoclave heating, microwave irradiation or sonication. The catalytic performances were evaluated by comparison with tests carried out using sodium methoxide. The experiments were carried out at 70 °C, under microwave, at room temperature, under sonication, and at 150 °C, in autoclave. In addition to the product analysis, leaching was checked in details for each experiment. After less than 90 min, the reaction carried out under microwave led to a near total conversion of the vegetable oils, with a near total selectivity in monoesters, irrespective of the vegetable source. The molar ratio methanol: vegetable oil was of 4:1, namely, very small. Under autoclave and sonication conditions the conversion was about 80%, with a selectivity to monoesters of about 90%. The reactions carried out under the microwave and autoclave led to a leaching less than 10 ppm of alkaline species, while under the sonication the leaching was about 5 wt% from the initial content. Under autoclave and microwave conditions the catalysts showed also a good recyclability.

References

- [1] Z. Zhang, R.W. Hicks, T.R. Pauly, T.J. Pinnavaia, *J. Am. Chem. Soc.* 124 (2002) 1592; Z. Zhang, T.J. Pinnavaia, *J. Am. Chem. Soc.* 124 (2002) 12294.