## Porosity of clay catalysts for biomass conversion: a comparative study

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Clay derived materials are environmentally friendly catalysts that can be quite easily tailored to optimize the catalytic activity for a precise reaction of interest among a wide variety of organic reactions [1]. This can be achieved through appropriate modification treatments of the clays, which include acid activation and ion exchange. For example, in previous work, we found that acid treatment of materials derived from a bentonite (SD) collected at Porto Santo Island, part of the Madeira Archipelago, exhibited high catalytic activity in the oxidation of limonene to *p*-cymene [2]. Besides the introduction of catalytic sites, alterations in the porosity usually occur upon the modification treatments, the extent of which depend on the specific conditions and also on the nature of the starting clays, and can be determinant for the catalytic performance, such as for selectivity. We are using acid activated and ion exchanged clay minerals, from different origins, as solid catalysts in other reactions, such as the methoxylation of limonene and the conversion of glycerol, for which the knowledge of the role of the porosity is necessary. Although considerable improvements of the textural properties are achieved with the treatments, it is known that a detailed description of the porosity, in particular of microporosity, from the analysis by nitrogen adsorption at 77 K alone, is not straightforward [3] and we have shown that n-nonane pre-adsorption method, with adaptations, can provide valuable information about the microporosity of acid activated clays [4]. Therefore, we have also been using this method for elucidating the complex porosity of ion exchanged clay minerals, from different sources, and after acid activation under different conditions. The results, to be reported in the communication, allowed us to obtain a clear comparison of the effects on the porosity of the chemical treatments on clays from the Source Clays Repository (USA) and SD clay from Porto Santo (Portugal) where a large amount is readily available.

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## References

- 1. Adams, J. M.; McCabe, R. W. *Clay Minerals as Catalysts*, in Bergaya, F.; Theng, B.K.G.; Lagaly, G. (Eds.) *Handbook of Clay Science*, Elsevier, Amsterdam, 2006, p. 541.
- 2. Fernandes, C.; Catrinescu, C.; Castilho, P.; Russo, P.A.; Carrott, M. R.; Breen, C. Appl. Catal. A 2007, 318, 108.
- 3. Rouquerol, F.; Rouquerol, J.; Sing, K. Adsorption by Powders and Porous Solids, Academic Press, London, 1999.
- 4. Ribeiro Carrott, M. M. L.; Cansado, I. P. P.; Russo, P. A.; Carrott, P. J. M.; Catrinescu, C.; Castilho, P.; Fernandes, C.; Breen, C. Porosity of acid activated Porto Santo bentonites assessed by n-nonane pre-adsorption and nitrogen adsorption, in Catalysis: from the active site to the process, Symposium in Honour of Ramôa Ribeiro, IST, 2012, p. 28.