Invitation à la soutenance publique de thèse de
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Pour l'obtention du grade de Docteur en sciences agronomiques et ingénierie biologique

« Friedel-Crafts alkylation of resorcinol with methyl-tert-butylether immobilized over Keggin tungstophosphoric acid heterogeneous catalysts »

qui se déroulera
le vendredi 07 juin 2019 à 16h
Auditoire LAVO 51
Place Louis Pasteur, 1
1348 Louvain-la-Neuve

Membres du jury :
Prof. Eric Gaigneaux (UCLouvain), promoteur
Prof. Yann Garcia (UCLouvain), président
Prof. Sophie Hermans (UCLouvain), secrétaire
Prof. Olivier Riant (UCLouvain)
Prof. Hermenegildo Garcia (Universidad Politecnica de Valencia, Espagne)
Prof. Joeri Denayer (VUB)

Alkylated resorcinols are important as antioxidant and widely used in the pharmaceutical and fine chemical industries. 4-tert-butyleresorcinol is used as active component in the treatment of skin diseases and as colour developer.

Resorcinol alkylation to 4-tert-butyleresorcinol is an electrophilic aromatic substitution, traditionally carried out in homogeneous phase using strong Brensted acids (e.g., H₂SO₄). The increasing environmental concern raised the issue of developing sustainable alternatives. The use of heterogeneous solid catalysts would reduce the amount of wastes produced since they can be easily separated from the reaction mixture by filtration. However, despite the important role of alkylated dihydroxybenzenes in the chemical industry, only few works involving the use of heterogeneous catalysts have been carried out in the last years. Even though resorcinol conversion was kept high (up to 99%) the selectivity to 4-tert-butyleresorcinol were low, because of the formation of the di-alkylated product 4,6-di-tert-butyleresorcinol. In addition, previous works have missed to address attention to the reaction mechanism at the catalyst surface. Further, the impact of the catalyst surface chemistry on the reaction was not investigated enough.

In this context, this research project aims at answering the question: how to obtain 4-tert-butyleresorcinol with good resorcinol conversion and high selectivity in a clean way?

The resorcinol alkylation reaction mechanism and the catalyst surface chemistry are at the core of this research. Keggin phosphotungstic acid (HPW) was chosen as active phase to catalyse the resorcinol tert-butylation. To be used in a polar liquid environment, it was heterogenized by immobilization using the hydrolytic sol-gel method following two different approaches: the not-templated synthesis and the templated synthesis using surfactants. In the first group of catalysts, obtained with the not-templated approach, different supports (SiO₂, TiO₂ and ZrO₂) were tested to establish the different interactions of the HPW with the oxide matrices and the consequences on the catalytic activity. The reaction mechanism was investigated, and the reaction path defined in different reaction conditions: the resorcinol alkylation was carried out in the temperature range from 60 °C to 80 °C degrees in absence or in presence of solvents.

Through templated sol-gel method, the tuning of the catalyst surface chemistry was investigated, especially in terms of acidity (Brensted and Lewis acid sites) and in terms of the affinity of the reagents and products for the catalyst surface itself.

The Brensted acid sites % was found to play a crucial role in the resorcinol conversion, which was found to increase and then to decrease when the Brensted % increased, reaching a maximum when the optimal Brensted % of 26% was attained. Resorcinol tert-butylation resulted in a mixture of mono and poly-alkylated products and ethers. The selectivity to the mono-alkylated 4-tert-butyleresorcinol could be enhanced adjusting the % of Brensted acid sites at the catalyst surface as well: the selectivity increased from 24 to 41% when the B sites % decreased from 64% to 42%.

Using tetrahydrofuran as solvent during the reaction boosted further the selectivity to 4-tert-butyleresorcinol to 74% when the reaction was carried at 60 °C and up to 99% when the temperature was increased to 80 °C.