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Ru/TiO₂-based catalysts for the hydrogenation of levulinic acid using formic acid as an internal hydrogen source

ABSTRACT

Value added platform molecules issued from the conversion of lignocellulosic biomass feedstock are expected to play a pivotal role in the move towards future 'renewable-based chemicals' biorefinery schemes. Especially γ -valerolactone (GVL) has attracted a significant attention in the recent decade due to its versatile applications. GVL can be obtained by catalytic hydrogenation of levulinic acid (LA) issued from the hydrolytic conversion of lignocellulosic biomass using pressurized external source of hydrogen. However, more sustainable approach is to utilize hydrogen originating from the decomposition of formic acid (FA) that is formed in an equimolar mixture with levulinic acid during the acidic hydrolysis of lignocellulosic biomass. This is more challenging, since the strategy requires that both the hydrogenation of LA to GVL and the FA dehydrogenation can be catalyzed by a single material in similar reaction conditions.

Therefore, the main objective of this PhD work is to develop active and selective catalysts based on titania supports for the one-pot hydrogenation of levulinic acid to γ -valerolactone with internal hydrogen transfer supply via the in-situ decomposition of formic acid as well as to define the properties/activity relationship driving the performance of the catalysts in the studied reactions.

In this work, a modification of the titanium oxide support was proposed in order to increase the catalyst selectivity in the decomposition of formic acid towards hydrogen. In addition, an alternative method of deposition of the active metallic phase on the support has been proposed, which allows to obtain very small ruthenium particle size with a narrow particle size distribution, additionally permits to precisely tune the particle size of Ru.

The bibliographic part presents the information regarding levulinic acid and γ -valerolactone, the catalytic systems used for LA hydrogenation and dehydrogenation of formic acid. A large part of this chapter is also devoted to the role of the support, influence of the basic sites and effect of metal particles size on the catalytic activity in studied reactions and different methods for controlling the size of Ru particles.

The experimental part is devoted to the catalysts' preparation protocols and the details regarding the analytical techniques employed for the investigation: X-ray diffraction, N₂ physisorption, isoelectric point measurements, FTIR-CO chemisorption, inductively coupled plasma atomic emission spectroscopy, temperature programmed reduction, transmission electron microscope, scanning electron microscope, X-ray photoelectron spectroscopy and time of flight secondary-ion mass spectrometry. Moreover high-performance liquid chromatography and gas chromatography were used for the analysis of the reaction products.

In the first part of work, titanium oxide was modified by doping with calcium ions during the sol-gel synthesis method for elaborating titania-based mixed supports. Materials with different calcium content (0, 1, 5, 10 and 20 wt. % in respect to TiO₂) were obtained, and were analyzed by X-ray diffraction analysis and N₂ physisorption. Based on the obtained results, it was found that as a result of the modification, the specific surface area of the carriers was increased and in the case of larger amounts of calcium the presence of a new crystallographic phase of calcium titanate CaTiO₃ was observed. In addition a change in the anatase cell parameters which resulted in the change of the anatase cell volume suggesting that some amount of calcium ions were incorporated into the crystal lattice of TiO₂.

Significant part of the work was focused on the development of the innovative method for obtaining heterogeneous catalysts with the use of sunlight. The method of photodeposition, although it has been known before, was not usually used to introduce ruthenium. Process conditions were optimized by determining the mechanism of photodeposition using two ruthenium precursors (RuCl₃ and Ru(acac)₃), the effect of the precursor, its concentration on the rate of photodeposition and the properties of the obtained catalyst were determined. In addition, it was demonstrated that by utilizing photodeposition method it was possible to precisely control the size of the ruthenium particles depending on the conditions of the deposition process. A great success was the development of the process conditions that allow to obtain 5 wt. % Ru on titanium oxide, which has not been achieved before. Those catalysts were compared to the materials prepared by the conventional wet impregnation method and it was found that by using photo-assisted method, much smaller Ru sizes, uniformly dispersed on TiO₂ with a very narrow particle size distribution, could be obtained. Moreover, in contrast to the impregnation, the photodeposition method does not require any additional step in the form of sample reduction in hydrogen flow at elevated temperature.

The next step of the work was to determine the catalytic activity of the obtained catalysts in the hydrogenation of levulinic acid using formic acid as an internal source of hydrogen, and separately in hydrogenation reactions of LA using molecular hydrogen and the decomposition of formic acid in the liquid and gas phase. It has been shown that the controlled modification of the TiO₂ support by calcium addition improved the catalytic performance in both the FA dehydrogenation step and the LA hydrogenation reaction. Such modification resulted in a decreased anatase crystallite size, together with the formation of a new calcium titanate phase, leading to the stabilization of smaller ruthenium

particles on the support. Stronger interaction of ruthenium with the support was observed, which affected the strength of CO adsorption on the surface of the Ca-modified catalyst, thus facilitating the reaction performance. The role of calcium is also related to the increased basicity of the catalyst surface, which had a positive effect on the catalytic activity in the studied reactions. In addition, much better results in both reactions were achieved using catalysts obtained by the photodeposition which was possible owing to the formation of uniform, small and well-dispersed metal nanoparticles as well as the change in the interaction between the metal and the carrier.

In summary, Ca-modified TiO₂ supported Ru catalysts exhibited improved activity in the formic acid decomposition and levulinic acid hydrogenation when compared to Ca-free samples. This was caused by stronger interaction of the ruthenium with the support and consequently weaker adsorption of CO on the active sites as well as by the increased basicity of the material. In addition, significant improvement in catalytic performance was achieved by using an alternative catalyst preparation method, that was optimized for depositing large loadings of ruthenium and which resulted in uniformly dispersed ruthenium nanoparticles of much smaller size than those obtained by the impregnation method.

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