



**BORATED ZIRCONIA PREPARED USING DIFFERENT ZIRCONIUM AND BORON
PRECURSOR CONCENTRATIONS AND CALCINATION TEMPERATURES AS
CATALYST FOR ALCOHOL ACETYLATION WITH ACETIC ACID**

M.N. Blanco, L. Osiglio, G. Romanelli

*Centro de Investigacion y Desarrollo en Ciencias Aplicadas "Dr. Jorge J. Ronco" (CINDECA),
Departamento de Quimica, Facultad de Ciencias Exactas, Universidad Nacional de La Plata-CCT
La Plata, CONICET, 47 N° 257, 1900 La Plata, Argentina*

mnblanco@quimica.unlp.edu.ar

The protection of –OH groups by acetylation is one of the most common methods employed in synthetic organic chemistry and provides an efficient route for the synthesis of compounds with industrial value, such as medicines, fragrances, food preservers, plasticizers and cosmetics. Different catalysts have been reported to be suitable for carrying out this type of transformation, such as mineral acids, polyoxometallates, Ti, Sn or Hf salts, aluminum phosphate on molecular sieves, Amberlist-15, ionic exchange resins, and Lewis acids such as Cu or Sc triflates, CoCl₂, TaCl₄, among others. The preparation of some of these catalysts is difficult and on several occasions secondary reactions are produced. The classical procedures based on mineral acids such as sulfuric or fluorhydric acids cause environmental, corrosion and toxic problems.

On the other hand, the system formed by zirconium oxide doped with boron (borated zirconia) is a solid with acid characteristics that has been used in a variety of organic reactions, such as Beckmann rearrangement of cyclohexanone oxime, anisole benzylation, transesterification of β -ketoesters, and C-methylation of phenol with methanol.

In the present work, the use of borated zirconia as catalyst in the acetylation of alcohols and phenol was studied. The catalysts were obtained employing the micellar method for the oxide synthesis and different preparation conditions. The concentration of the precursor in the solution used to obtain the oxide, the concentration of the boron precursor and the calcination temperature were varied. All the solids showed amorphous characteristics and strong acidity. Boron addition increased the temperature range of the hydrated oxide stability, which depends on the boron concentration in the



sample. Besides, the characterization by infrared spectroscopy showed that in the samples with high boron content, small B₂O₃ aggregates are present, in addition to boron species interacting with the support observed at a lower boron concentration. The three preparation conditions under study affected the textural properties of the catalysts, as well as their acid strength.

There was a good agreement between the yield of acetylated product obtained in the acetylation of 2-phenoxyethanol and the acid strength of the catalysts, using acetic acid as acetylating agent, toluene as reaction solvent and reflux temperature. The best yield of acetylated product (80%) was achieved with the catalyst containing 15 g B₂O₃/100g of a support obtained using a high concentration of ZrOCl₂ precursor in the starting solution used to prepare the oxide (0.56 mol Zr/dm³) and a relatively low calcination temperature (320 °C). The catalysts can be reused, as they maintained almost the same activity after three reuse cycles. Another primary alcohol, phenyl ethanol, showed similar behavior, whereas benzylic alcohols and phenol led to lower yields. In all the studied reactions, the acetylated product was obtained with a high selectivity because almost all the unconverted alcohol or phenol was recovered. So, the methodology employed is a green alternative for acetylation reactions, tending toward eco-efficiency due to the use of relatively cheap catalysts and, also, because water is obtained as byproduct of the reaction when acetic acid is used as acetylating agent in replacement of the traditional agents.