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Furfural aldolisation by acetone over magnesium hydroxide fluorides as promising basic catalysts, towards the valorization of hemicellulose to biofuels

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PURPOSE OF THE ABSTRACT

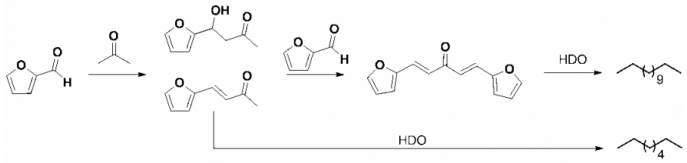
The valorization of ligno-cellulosic biomass is one of the important routes chosen by the European Union to control the consumptions of non-renewable resources and to fight against climate change. Thus, the search for new methods of producing fuels from renewable raw materials is a major challenge for the scientific community. In this context, wastes from ligno-cellulosic material, especially hemicellulose, are extremely interesting resources [1]. Furfural, resulting from the depolymerization of this polymer, is often considered as an extremely interesting platform molecule. For example, this compound, after a condensation reaction with a molecule of acetone followed by a deoxygenation reaction, can lead to the production of new biofuels containing hydrocarbons with 8 and 13 carbon atoms (Scheme 1) [2]. The first transformation can be carried out by an aldolization reaction, known to be catalyzed by basic solids [3]. The elimination of oxygen atoms can be carried out by a hydrodeoxygenation (HDO) reaction, known to be catalyzed by different active phases like sulphides, metals or phosphides [4,5].

During this study, we were interested of the aldolization reaction of furfural by acetone carried out under mild conditions (50 °C, Patm). Different magnesium hydroxides fluorides exhibiting both acid-base properties and high surface area were evaluated as catalysts.

Thus six solids with different F / Mg ratios (0 to 2) were prepared by a sol-gel method in order to modify their acid-base properties [6]. All solid samples were fully characterized using different techniques (nitrogen adsorption, electron microscopy, Infra-Red, XRD, ATD-ATG). From CO2 adsorption followed by IR experiments, a basicity scale was established: MgF1.5(OH)0.5 > Mg F(OH) ~ Mg F1.75(OH)0.25 > MgF0.5(OH)1.5 > Mg(OH)2 >> MgF2. The order of activity measured in the aldolization of furfural by acetone was in perfect agreement with the differences in the basicity of these solids (Fig. 1). A mechanic mixture composed of 25% Mg(OH)2 and 75% MgF2, leading to the same F/Mg ratio as the most active catalyst, gave a very poor activity. It showed that the activity of MgFx(OH)2-x catalysts is linked to the proximity of acid (probably vacancy on Mg) and basic (probably OH groups) sites presents on magnesium hydroxide fluorides.

To conclude, this study clearly shows that magnesium hydroxide fluorides could become catalysts of choice for reactions requiring basic catalysis, as illustrated here by the aldol reaction.

FIGURES



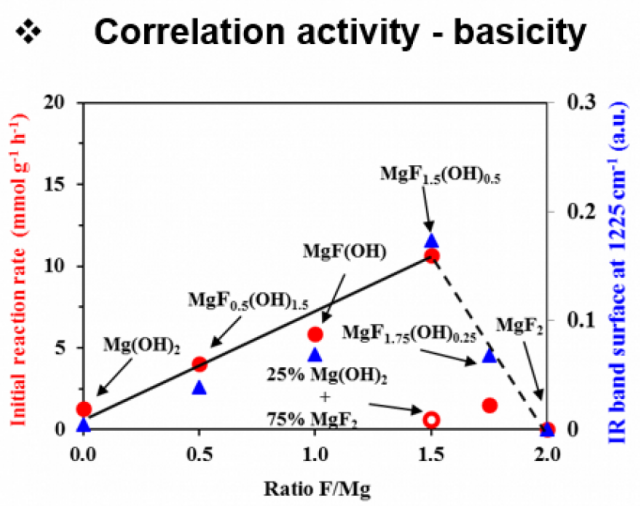


FIGURE 1

Scheme 1

Transformation from furfural to biofuels

FIGURE 2

Figure 1

Aldolization of furfural with acetone in the presence of different magnesium hydroxide fluorides

KEYWORDS

Aldolization | Furfural | Basic catalyst | Magnesium hydroxide fluorides

BIBLIOGRAPHY