Selective carbon deposition on γ-Al_2O_3 acid sites : toward the design of new stable catalysts for reactions in aqueous phase

GIREL Etienne[a], **CABIAC Amandine**[a], **CHAUMONNOT Alexandra**[a] , **TUEL Alain**[b], **BESSON Michèle**[b]

[a] *IFP Energies nouvelles, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France*
[b] *IRCELYON, 2 Avenue Albert Einstein, 69100 Villeurbanne, France*
Corresponding author: etienne.girel@ifpen.fr

1. Introduction

Transformation of lignocellulosic biomass requires operating conditions different from those used in refining and petrochemical processes. Several reactions are carried out in aqueous phase at temperatures above 200°C under high pressure. Conventional heterogeneous catalysts used for refining and petrochemical industries are usually prepared on porous supports with high specific surface areas such as alumina and silica. However, these catalyst supports are generally unsuitable for reactions carried out under these hydrothermal (HT) conditions due to structural and/or textural modifications[1,2], thus resulting in poor long-term catalytic performances.

Our work aimed to synthesize catalysts, which are stable under aqueous-phase conditions at elevated temperatures and are adapted to the treatment of new raw materials including biomass and its derived substrates. To achieve this objective, our strategy consisted of modifying the surface of a conventional γ-alumina support in order to make it more resistant to HT conditions. This surface modification was carried out with carbon as a surface additive. In this way, the favorable carbon surface properties are combined with textural and mechanical properties of alumina.

2. Experimental

High specific surface area γ-Al_2O_3 was prepared by calcination of commercial SASOL boehmite. Hydrothermal stability tests were conducted in a stainless steel autoclave at 200°C for 10 h under autogenous pressure (15 bars). The amount of AlOOH phase formed was calculated via XRD analysis. Detailed study of polyols (sorbitol, xylitol, glycerol, etc.) adsorption on alumina surface during the hydrothermal treatment was carried out. Polyols were directly introduced into the aqueous solution of the stability test using the same conditions as mentioned above. The amount of polyols adsorbed was determined by HPLC analysis of the liquid phase. Composites C/γ-Al_2O_3 were synthesized by conventional methods such as: (a) impregnation of sucrose followed by pyrolysis[3] and (b) chemical vapor deposition[4] (CVD) using EtOH as the carbon source. Finally, a new innovative synthesis pathway was developed using polyols selectively adsorbed on alumina acid sites as carbon source. The composites C/γ-Al_2O_3 were characterized by N_2 physisorption, TGA, FTIR, EtOH TPD, RAMAN spectroscopy, ^{13}C NMR spectroscopy and TEM. Ruthenium catalysts were prepared by wet impregnation of the various C/γ-Al_2O_3 supports with a a Ru precursor aqueous solution and reduction in a H_2 flow. Catalytic performances and deactivation were evaluated in the hydrogenolysis reaction of glycerol to 1,2 propanediol and ethylene glycol.

3. Results and discussion

We firstly investigated the hydrothermal stability of γ-Al_2O_3 when it was submitted to an hydrothermal treatment in the absence of any additive: γ-Al_2O_3 underwent hydration to form boehmite (γ-

$Al_2O_3 + H_2O \Rightarrow 2\ AlOOH$) with important modifications of its textural properties[2]. This transformation was complete after 90 min of treatment only.

We showed that it is difficult to protect alumina from hydration using carbon deposited via conventional methods. The homogeneity of the carbon deposit was better using gas phase carbonization than by impregnation/pyrolysis of sucrose. For both conventional synthesis methods, a high amount of carbon was necessary to effectively protect alumina from hydration (Figure 1) leading to a degradation of the textural properties of the original alumina (pore filling, lower specific surface area, etc.).

When polyols were introduced in the aqueous solution, they could adsorb on alumina surface and prevent it from hydration[5]. This effect increased with the carbon chain length of the polyol. We showed that adsorption of sorbitol and xylitol was selective on specific alumina surface sites. Alumina was already totally protected from hydration when only 20% of its surface was covered with sorbitol. Characterization of the sorbitol/alumina samples combined with a study using alumina solids with different morphologies (such as needles, plate-like or rods-like) suggested a localization of adsorption sites on the basal facets (110) of alumina platelets. Our study showed that to effectively protect alumina from hydration, the adsorbed polyol should exhibit specific properties in terms of carbon chain length, number of OH groups and stereochemistry.

Finally, using materials consisting of in-situ adsorbed polyols on alumina as the starting system, it was possible to synthesize $C/\gamma\text{-}Al_2O_3$ composite with carbon deposited selectively on the alumina primary hydration sites (basal facet 110). Such material provided increased hydrothermal resistance with only a low carbon content (Figure 1). Our results show that carbon localization is a key parameter to synthesize carbon/alumina composites stable in HT conditions. Only a limited amount of surface sites needs to be covered.

Ruthenium was deposited on those materials and the resultant catalyst was used for glycerol hydrogenolysis reaction. Catalyst deactivation was limited when carbon was selectively deposited on alumina support.

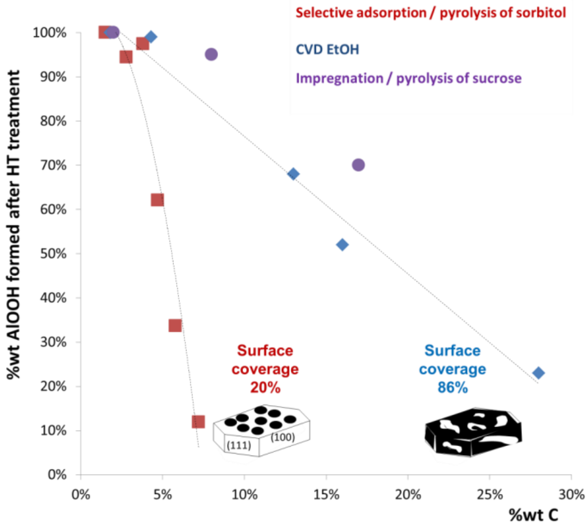

Figure 1 Amount of boehmite formed after HT stability test versus amount of carbon for samples prepared by CVD EtOH, impregnation/pyrolysis of sucrose, and selective adsorption/pyrolysis of sorbitol.

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