ISGC 2019 May 13rd - 17th

N°199 / OC
TOPIC(s) : Biomass conversion / Homogenous, heterogenous and biocatalysis

Water tolerant alumina based heterogeneous catalyst for biomass conversion

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PURPOSE OF THE ABSTRACT

1. Introduction

Production of some bio-products from lignocellulosic biomass derivatives are carried out under drastic operating conditions i.e. in liquid aqueous phase and at temperature above 200°C under high pressure (hydrothermal conditions). One can cite for example aqueous phase reforming or hydrogenolysis of polyols and sugars. Industrial heterogeneous catalysts used for refining and petrochemical applications are mainly supported on porous alumina and are unsuitable for reactions carried out under hydrothermal conditions. Indeed, structural and textural modifications of the support and metal sintering occurred, resulting in poor long-term catalytic performances [1, 2]. Our work aimed to synthesize hydrothermal compatible catalysts by designing water tolerant material as catalyst support. We thus have chosen to modify gamma-alumina surface by adding carbon additive. We particularly have investigated different methodologies to prepare the carbon/Al2O3 composites. The chemical nature and localization of the carbon deposit was evaluated by a multi-analysis methodology. The hydrothermal resistance was evaluated in an on purpose reactivity test. The most promising materials have been finally used as catalyst supports for glycerol hydrogenolysis.

2. Experimental

High specific surface area gamma Al2O3 was prepared by calcination of commercial SASOL boehmite. Composites C/Al2O3 with carbon content in the range 7 to 30%wt., were synthesized by three different methods : (a) impregnation of sucrose followed by pyrolysis under N2 atmosphere at 600°C, (b) chemical vapor deposition (CVD) using EtOH as the carbon source at 600°C and finally (c) innovative synthesis pathway using polyols as carbon source. The carbon composites properties were characterized by N2 physisorption, TGA, FTIR, RAMAN spectroscopy, 13C NMR spectroscopy and TEM. 3 wt. % Ru or Cu catalysts were prepared by wet impregnation with Ru(NO)(NO3) or Cu(NO3)2 aqueous solutions. Hydrothermal tests were conducted in a 100 mL stainless steel autoclave at 200°C for 10 h under autogeneous pressure (15 bar). Hydrogenolysis of glycerol was carried out in a 100 mL stainless steel autoclave at 200°C under 80 bar H2 pressure for 48h (0.2 g catalyst, 60 mL 100 g/L glycerol).

3. Results and discussion

Hydrothermal resistance of pure gamma-Al2O3 at 200°C is low : hydration to boehmite is completed in only 90 min. Textural and structural properties are strongly modified with a surface decrease from 212 m2/g to 50 m2/g. C/Al2O3 composites were first prepared by room temperature sucrose impregnation followed by pyrolysis under N2 atmosphere at 600°C. The carbon content was controlled by the sugar solution concentration. The nature of the carbon deposit is mainly aromatic (Raman analysis). High carbon content, around 30wt. %, is required to prevent boehmite formation during hydrothermal stability test. Textural properties of the resulting materials are thus strongly modified by C deposit with a drop in porous volume. The carbon content of C/Al2O3 composites prepared by CVD of EtOH was varied from 2 wt. % to 30 wt. % by experiment duration. As for sugar / pyrolysis materials only high carbon content prevented boehmite formation. The carbon is localized on the alumina facets without any selectivity. Using sorbitol as carbon additive led by an innovative method of preparation to hydrothermally stable C/Al2O3 composites. The carbon content required is only 7 wt. % C. The carbon localization is selective and a (110) basal facet localization is proposed. The 7% wt. C/Al2O3 support was tested in a glycerol solution at 200°C and stability was conserved even in reactive conditions.

4. Conclusions

Low carbon content and selectively localized C/Al2O3 composites were synthesized by an innovative method. This methodology is promising for the design of stable supports of heterogeneous catalysts for bio products synthesis.

FIGURES

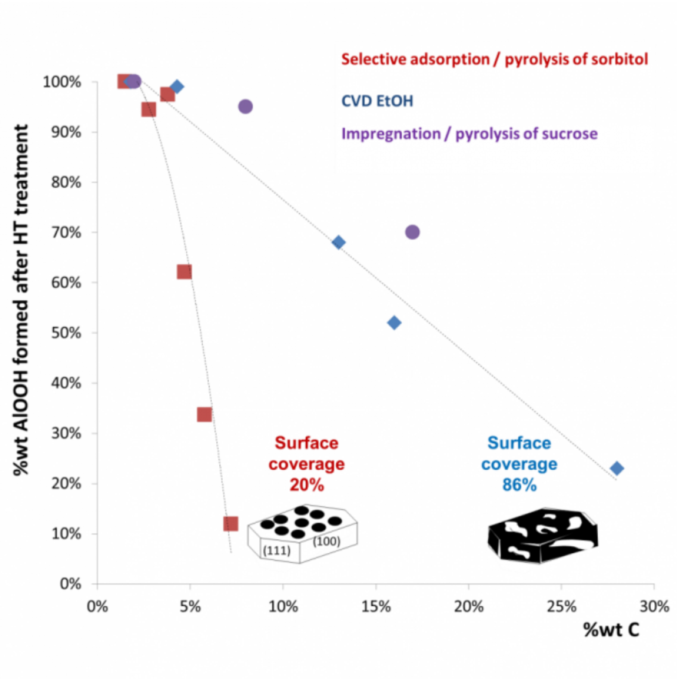

FIGURE 1

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.

FIGURE 2

KEYWORDS

C/alumina composite | hydrothermal stability | glycerol hydrogenolysis

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