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Efficiency of sulfonated reduced graphene oxide in the glycerol etherification with tert-butyl alcohol

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PURPOSE OF THE ABSTRACT

Abstract

Acidic heterogeneous catalysts can be used for the synthesis of di- and tri- tert-butyl-ether of glycerol (DTBG and TTBG, respectively) with tert-butyl alcohol (TBA). DTBG and TTBG, contrariwise to the monoether, are high octane oxygenated compounds useful for fuel applications. For more than a decade, research has focused on finding efficient heterogeneous acid catalysts for the etherification of glycerol with TBA. Zeolites [1] and ion exchange resins [2] have found great interest as solid catalyst presenting important activities in this reaction. Yet they present relatively low tolerance to water, which is a by-product of this reaction. A new catalyst that has attracted attention due to its tolerance to water [3] and which in additionally feature good catalytic behavior, is functionalized graphene oxide [4-6]. In this communication we evaluate the catalytic activity and selectivity of sulfonated reduced graphene oxide in the glycerol etherification with tert-butyl alcohol (T=363 K, TBA:glycerol molar ratio of 4:1 with 7.5 wt.% of catalyst)., Two methods of graphene oxide synthesis were performed: (i) the modified Hummers method [7] and (ii) the method reported by Marcano [8], with some variations, on the graphite as starting material. Three methods of graphene oxide reduction were subsequently applied: (i) reduction with hirazine hydrochloride (H) (ii) reduction with Zn/HCl (Zn) and (iii) reduction with ascorbic acid (AA). Functionalization was carried out by means of diazonisation with sulphanilic acid and sodium nitrate, (S), at room temperature. The structural, textural and acidic properties of each sample are characterized by XRD, nitrogen physisorption, Raman spectroscopy, electronic microscopy (SEM and TEM), XPS and elemental analysis.

Figure 1 compares the glycerol conversion as well as the selectivities into MTBG and DTBG on different catalysts. The glycerol conversion achieved with the sulfonated reduced graphene oxide is greater than that obtained with Amberlyst® 15 (A-15), reaching up to 78%, a value very close to the thermodynamic limit calculated in our study (80%). This is related to the greater tolerance of GO to water compared to the exchange resin A-15. The selectivity towards DTBG that is favored by the use of catalysts with high porosity as in the zeolites, is clearly reached by the GO. This could be related to the high density of sulphonic groups on the surface, besides it is possible to obtain sheets of graphene oxide in the order of nanometers, increasing the catalytic activity. The reduction route is fundamental to achieve the best results. Indeed, the reduction with ascorbic acid allows to achieve the highest etherification yields.

FIGURES

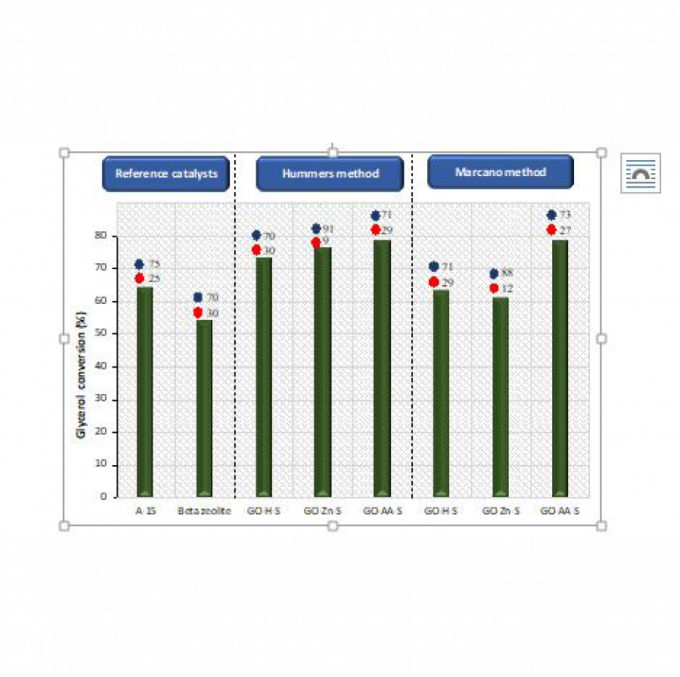

FIGURE 1

Figure 1. Glycerol conversion into MTBG and DTBG of various catalysts: Amberlyst 15, Beta zeolite and graphene oxide obtained by different methods.

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FIGURE 2

KEYWORDS

glycerol | graphene oxide | etherification | catalysis

BIBLIOGRAPHY