ISGC 2022

N°581 / OC
TOPIC(s) : Biomass conversion / Homogenous, heterogenous and biocatalysis

Hydrodeoxygenation of furfural to 2-methylfuran using supported Mo carbides

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PURPOSE OF THE ABSTRACT

The continuous use of fossil fuels, the growth of CO2 emissions and the increasing demand for chemicals and fuels have stimulated the search for alternative energy sources in recent decades. In this context, lignocellulosic biomass emerges as a potential substitute for petroleum, since it is abundant and presents low cost [1]. Furfural (FF) can be obtained directly from biomass and can be used to produce 2-methylfuran (2-MF), a versatile molecule that presents application as biofuel, fuel additive, solvent and as an intermediary in the synthesis of pesticides, antimalarial drugs, etc [2]. Recently, Deng et al. [3] demonstrated that unsupported Mo carbides are active and selective in obtaining 2MF, in addition to the fact that these materials exhibit comparable catalytic performance to noble metals such as Pt [4]. Taking into consideration that only unsupported carbides have been tested in the liquid phase HDO reaction of FF, it would also be interesting to evaluate the use of these materials dispersed on various supports. Therefore, the present work had as main objective to investigate the performance of Mo carbides supported on SiO2, TiO2, ZrO2 and ZSM-5 in the furfural hydrodeoxygenation reaction to produce 2-methylfuran.

The catalysts were prepared by incipient wetness impregnation to achieve 20 wt.% Mo2C. After impregnation, the samples were heat treated at 500 ºC (5 ºC/min) / 3 h under static air and then synthesized by temperature programmed carburation at 650 ºC (2.5 ºC/min) / 2 h with 20 % CH4/H2. After that, they were passivated for 14 h with 0.5 % O2/N2. The HDO reactions were carried out in a batch reactor at 200 °C for 4 h under 30 bar H2 using a stirring of 600 rpm and 2-butanol. Prior to the catalytic evaluation, the Mo catalysts were reactivated at 400 °C (5 °C/min) / 1 h at 30 bar H2. The reaction products were analyzed by GC (Agilent, model 7890, 5975C) using VF-WaxMs capillary column. The catalysts were characterized by ICP-OES, elemental analysis, XRD, N2 physisorption, TPR, NH3 desorption, FTIR of pyridine and XAS.

Under the reaction conditions used only a certain amount of FF is converted over SiO2, while for the supports presenting acid properties (TiO2, ZrO2 and ZSM-5) a higher conversion of FF was obtained, which indicates that they are capable of dehydrogenating 2BuOH to generate 2-butanone and hydrogen necessary to convert FF. For the Mo carbides a complete conversion of FF was observed with exception of Mo2C/ZSM-5, which showed a conversion of 82 % (Fig. 1). 2-Methylfuran was mainly produced over Mo carbide supported on SiO2 (68 %), TiO2 (59 %) and ZrO2 (60 %). FF is hydrogenated to furfuryl alcohol (FA), which undergoes hydrogenolysis to form 2MF [2]. The 2,2-(1,2-ethenediyl)bis-furan (EBF) is a C10 compound produced by dimerization of two FF molecules [3]. The 2-(sec-butoxymethyl)-furan (SBMF) is an ether obtained by reaction of FA with 2-butanol [5]. Meanwhile, the production of 2-(furan-2-ylmethyl)-5-methylfuran (FMMF) occur mainly by the reaction of FA with 2MF [6]. Finally, 5-hydroxypentan-2-one (HPTE) is formed through FF ring opening, which seems to occur in the presence of acid sites, since the formation of this compound was not observed in the Mo2C/SiO2 catalyst. These preliminary results show that the use of a non-acidic support such as SiO2 reduces the formation of compounds

formed on acid sites (SBMF and HPTE), which increases the production of 2MF. The comparison of catalysts with bare supports shows that when carbides are supported there is a significant change in the product distribution. FA was the main product on SiO2, TiO2 and ZrO2, whereas it is 2MF over the carbidic phase. Meanwhile, many by-products were observed over ZSM-5 and Mo2C/ZSM-5 due to the strong acidic nature of these materials. In any case, the Mo carbide supported on silica was the most suitable for the production of 2MF showing a higher activity and selectivity.

FIGURES

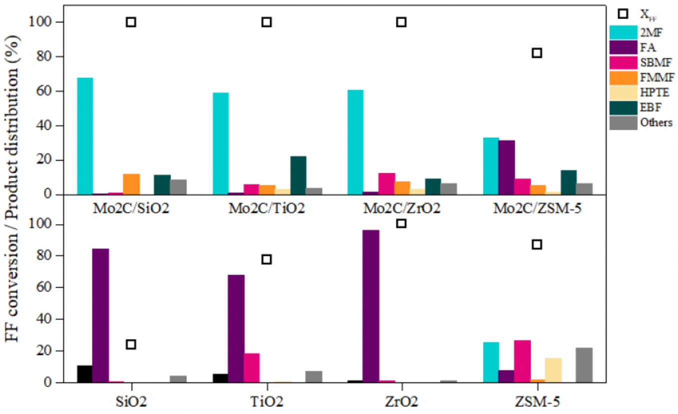

FIGURE 1

Figure 1

FF conversion and product distribution for Mo2C supported on different materials (reaction conditions: 200 °C, 30 bar H2, 4 h, 2-butanol).

FIGURE 2

KEYWORDS

Hydrodeoxygenation | Furfural | 2-methylfuran | Mo carbides

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