Nb-Beta zeolite catalysts for the efficient transformation of glucose to multiple platform molecules

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Abstract: Nb-Beta zeolites were prepared by a post synthesis methodology and investigated in the transformation of glucose. They contain residual framework Al-acid sites, extra-framework isolated Nb(V) and Nb_2O_5 pore-encapsulated clusters. Working in a biphasic water/ methyl-isobutyl-ketone (MIBK) solvent and in the presence of NaCl allowed the dehydration of glucose with a selectivity to HMF of 81% for a conversion of 44%. Under oxygen pressure and in hot water, the same materials acted as bi-functional catalysts affording dehydration of glucose to levulinic acid (LA) which, further, suffers an oxidation process to succinic acid (SA), with a selectivity as high as 84% for a total conversion of glucose.
Keywords: niobia, zeolite, glucose, HMF, succinic acid.

1. Introduction

The use of the biomass as feedstock is of a high current interest for the chemical industry since it ensures the sake of resources sustainability.[1] However, to answer the complexity and diverse reactivity of the various biomass substrates, it is necessary to develop novel catalytic systems able to afford the required high conversions of the feedstocks.[2] Several properties such as the particularly well dispersed high Brønsted acidity in the crystalline matrix and the controlled porosity at the molecular dimensions recommend synthetic zeolites as potential candidates in this attempt.[3] Zeolites with a high stability in hot liquid water can be achieved either by the treatment with mineral acids or through the insertion of a heteroatom in the hydrophobic dealuminated zeolite framework.[4]

In this work we focused our interest to a post synthesis strategy for the production of highly dispersed Nb species (0.02-0.05 moles%) into the Beta zeolite matrix. The obtained catalysts display excellent performances in the glucose transformation to different platform molecules, such as HMF and succinic acid, the selectivity depending on the reaction conditions.

2. Experimental

Nb-Beta zeolites were prepared through a two-steps post synthesis methodology. It involve the dealumination of a H-Beta zeolite with HNO_3 followed by impregnation with an isopropanol solution of Nb ethoxide ($Nb(OC_2H_5)_5$). The resulted solid was washed in distilled water, dried in air and calcined in static air atmosphere. The prepared samples were denoted as *Nb(x)-BetaN*, where x = 0.02 and 0.05 mol% Nb, and N = 12, 18 and 37 (*ie,* Si/Al ratio). The catalysts were characterized using different techniques such as: adsorption-desorption isotherms of nitrogen at -196 °C, TG-DTA, XRD, NH_3-TPD, DRIFT and XP spectroscopy, and ICP-OES. The catalytic tests were carried out in a batch mode under a vigorous stirring considering the following procedure: the catalyst was added to a solution of glucose in water and, after closing, the autoclave was heated up at 180°C for 12-24 h. Similar tests were made under molecular oxygen pressure (12-18 bar). Additional catalytic tests were also conducted in aqueous solutions of NaCl and MIBK. The reaction products were analyzed by GC-FID chromatography and the product identification was made by using a GC-MS Carlo Erba, Instruments QMD 1000.

3. Results and discussion

To date only scarce examples of Nb-based zeolites have been reported as active catalysts. Nb incorporated in the Beta zeolite framework were prepared, for instance, in a fluoride medium[5] while the

impregnation of zeolites only generates extra-framework niobium oxide species.[6] In accordance to the XRD and DRIFT characterization results the *Nb(x)-BetaN* zeolites contain residual framework Al-acid sites, extra-framework isolated Nb(V)O-H species linked by Nb-OSi bonds to the zeolitic walls, Nb_2O_5 pore-encapsulated clusters and Al−O extra-framework species. As NH_3-TPD analysis showed, the residual extra-framework aluminum species exhibit a stronger acidity. Moreover, such species prevent a further solubilization of the zeolite framework in hot water, as recently Sels and coworkers showed [7]. Also, the presence of the Nb species generated acid sites with moderate strengths and participates to the zeolite stabilization, most probably by polarizing the framework.

The dehydration of glucose to HMF in a biphasic water/MIBK solvent confirmed the role of the acidity of the new catalysts that was corroborated to their mesoporous texture (81% MHF for a conversion of glucose of 44%) (Figure 1).

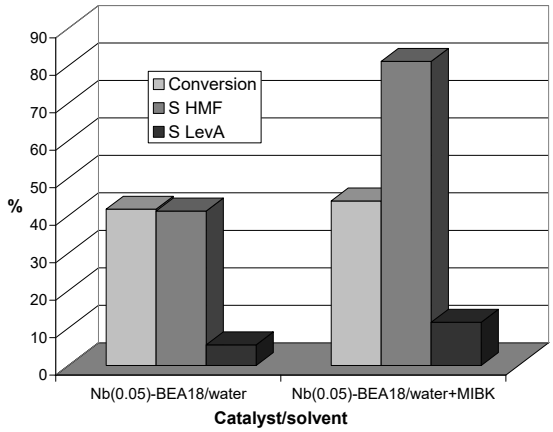

Figure 1. Catalytic performances of Nb(0.05)-Beta18 catalyst in water and water/MIBK biphasic solvent.

These new catalysts also showed a high efficiency for the one-pot oxidation of glucose to succinic acid.The mechanistic studies carried out in this study suggested that the dehydration glucose to LA is merely catalyzed by the extra-framework aluminum species. Further oxidation to SA is catalyzed by the Nb species. Thus, in the presence of the Nb(0.05)-β37 catalyst at 180°C, 18 bar of O_2, and after 12h, SA has been produced with a selectivity of 84%, for a total conversion of glucose.

4. Conclusions

Bi-functional Nb-Beta zeolite materials were produced via a post-synthetic insertion of Nb in the zeolite matrix. In a biphasic H_2O/MIBK solvent system and in the presence of NaCl glucose is efficiently dehydrated to HMF. Very important, this method allows an easy separation and reusability of the reactive aqueous phase containing the spent catalysts. Under oxygen pressure and in hot water, the glucose is dehydrated to LA which, further, suffers an oxidation SA. The novel catalysts can, therefore, serve as an attractive alternative to the previously developed catalysts based on the Ru critical element for the oxidation of glucose to SA. The novel catalysts also demonstrated a very good stability against water.

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