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Nb-based zeolites nanocomposite for glucose dehydration to HMF

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PURPOSE OF THE ABSTRACT

Furan-2,5-dicarboxylic acid (FDCA) is a promising biomass-derived chemical with wide applications in different industrial segments. Most important, FDCA is an extremely high potential platform chemical which can substitute the petrochemical derived terephthalic acid (PTA) in the production of polyesters [1, 2]. Therefore, the direct FDCA catalytic synthesis will have a huge economic benefit in the future and will play a vital role in the development of the sustainable chemistry. Such a vision requires, however, the development of a cost effective and industrially viable oxidation of HMF to FDCA able to operate in concert with the necessary dehydration processes of cellulose to HMF. Nevertheless, a primary technical barrier in achieving this vision is the development of an effective and selective sugars dehydration process to HMF. Therefore, to date, the direct synthesis of FDCA has been scarcely analyzed in the literature [3] taking care merely on individual steps occurring in the treatment of biomass. Thus, for the HMF synthesis from hexoses a large variety of heterogeneous catalysts like zeolites [4], ion-exchange resins [5], heteropoly acid salts [6] and sulfated and phosphoric acid-treated metal oxides [7, 8] were used. However, these methodologies have several disadvantages. Thus, besides HMF and other water soluble products, unwanted HMF aldol-condensation by-products, generically called "humins", are obtained in high amounts. To eliminate these we have to make face to a twofold challenge: (i) to suppress the formation of humins by developing efficient catalytic systems able to improve the yield of HMF [8] or (ii) to valorize the produce humins.

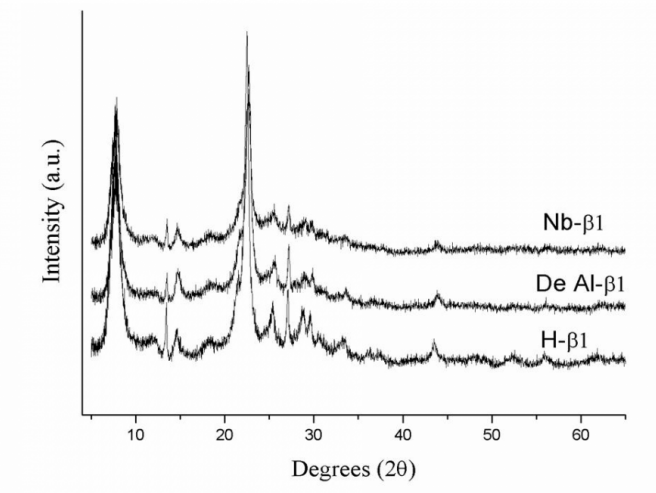
In this context, herein we present the two step synthesis of a series of Nb(1.6wt%)-Beta zeolites consisting in i) dealumination of Beta zeolite, and ii) isomorphic substitution. The catalysts were exhaustively characterized using XRD, Raman and DRIFT spectroscopy, ICP-OES and CO2- and NH3-TPD. Activity tests were carried out using glucose as raw material in an aqueous phase, in the temperature range 150-210°C for 24 h. For comparison, commercially H-BEA zeolites with different Si/Al ratios (18 - BEA 1; 6 - BEA 2; 12 - BEA 3) were also tested.

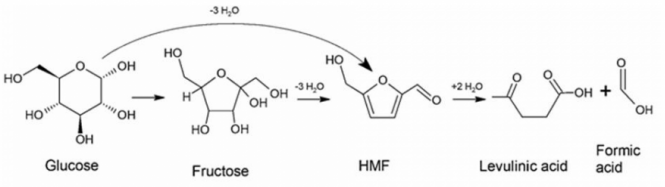
The X-ray diffraction patterns of the H-BEA samples display characteristic sharp and intensive reflections, at 2theta = 7.6°, 21.2° and 22.4°, indicating the well-developed crystalline structure of BEA topology. Dealumination by nitric acid did not affect the crystallinity, (see Figure 1, for exemplification) but the narrow diffraction line slightly shifted from 22.5 to 22.7°. This shift is assigned to the incorporation of Nb in dealuminated Si-BEA, leading to an expansion of the matrix due to the longer Nb-O bond distance (1.89 Å for tetracoordinated Nb(V) species in BEA zeolite) as compared to that of Si-O (typically 1.60-1.65 Å in zeolites). Structural modifications induced by Nb in the zeolite framework were also evidenced by FTIR spectroscopy. Shortly, the new FTIR small intensity band at 3743 cm-1 for Nb-BEA materials can be related to the presence of the Nb(V)O-H groups in the zeolite-like framework, in perfect accordance with [9]. The presence of the Nb(V)O-H groups is also supported by the new band at 952 cm-1 in the spectra of Nb-BEA materials. Although its origin is still under discussion, it is generally taken as an indication of the presence of Si-O-Nb units in the framework [10]. CO2- and NH3-TPD profiles also revealed high density acid/base sites, while the ICP-OES proven the stability of the new zeolites in hot water.

The Nb-based catalysts are efficient for the selective dehydration of glucose to HMF (Figure 2). The optimum

catalyst and optimal reaction conditions as well as the catalytic performances - catalytic properties correlation reveling the most promising Nb-BEA zeolite catalyst with the ideal features for the efficient HMF synthesis will be discussed in detail.

FIGURES





Catalyst	Si/Al ratio	T (°C)	Conv (%)	S_{HMF} (%)	S_{LA} (%)
H-β3	12	180	83.9	3.2	70.7
Nb-β3	-	**180**	**14.0**	**36.8**	**15.6**
H-β1	18	180	72.8	7.8	65.6
Nb-β1	-	**180**	**22.1**	**11.3**	**53.6**
H-β2	6	180	71.7	17.2	42.3
H-β2	6	150	3.8	52.6	0
H-β2	6	210	89.0	0	36.2

FIGURE 1

figure 1

X-ray diffraction patterns of H-?1, De Al-?1 and Nb-?1 samples

FIGURE 2

Figure 2

Selected catalytic results for the glucose dehydration

KEYWORDS

Niobium | zeolites | glucose dehydration | HMF

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