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Research Paper

Desilicated NaY zeolites impregnated with magnesium as catalysts for glucose isomerisation into fructose

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ABSTRACT

The impact of desilication on the performance of a series of alkali-treated NaY zeolites impregnated with 5 wt.% of magnesium for glucose isomerisation into fructose has been studied. Desilication at different NaOH concentrations increases the mesoporous volume and external surface area, without compromising microporosity and crystallinity. The observed reduction of the microporous volume due to magnesium impregnation was found to decrease for the alkali-treated zeolites. Higher density and strength of basic sites and stronger magnesium-support interaction were also achieved with the treatment. These improved properties resulted in a significant increase of both glucose conversion and fructose yield on the magnesium-doped desilicated zeolites. Glucose conversion continuously increases with desilication (28–51%), whereas fructose yield passes through a maximum (35%) at low desilication levels. Among the prepared desilicated samples, low-severity alkali-treated zeolites also show lower deactivation in consecutive reaction runs, as well as superior regeneration behaviour. Thus, hierarchical NaY zeolites impregnated with magnesium could be favourably used for glucose isomerisation into fructose if suitable alkaline treatment conditions are selected, with low-severity treated NaY zeolites being the best choice. Higher fructose productivities were achieved for the low-severity desilicated zeolites than for higher magnesium content NaY zeolites reported previously, leading to a lower Mg requirement.

1. Introduction

Increasing environmental concerns about the use of fossil fuels in the refining and petrochemical industry has turned worldwide efforts towards the development of processes based on renewable energy resources. Lignocellulosic biomass, a cheap, abundant and sustainable carbon source, has been a focus of attention from both industry and academia due to its great potential to be converted into fuels and value-added chemicals [1–4]. This has raised the interest in the study of saccharides transformations, mostly glucose, which is the main lignocellulosic biomass monomer [1,3,5–7]. A new range of applications for glucose have been investigated, such as its use as a raw-material for the production of fuels, important platform chemicals and polymers [1,3,8,9].

Glucose isomerisation into fructose is one of the key reactions in the biomass-derived glucose transformation chain for the production of chemicals and polymers, since fructose is an important starting material in the synthesis of numerous valuable bio-based compounds, such as levulinic acid, lactic acid or 5-hydroxymethylfurfural (HMF) [10–13]. The latter is a possible precursor for the production of caprolactam, the monomer for nylon-6 [14], while levulinic acid can serve as precursor for production of adipic acid [15].

Immobilised enzymes (D-glucose or xylose isomerase) have been traditionally applied as industrial catalysts for the isomerisation of glucose into fructose [16,17]. However, the search for a suitable chemical catalyst is essential for biomass valorisation, as it would make the process economically more attractive. Heterogeneous catalysts, in particular, present the advantages over homogeneous catalysts of being environmentally cleaner, more cost-effective and more easily regenerated and recycled. Basic solid materials were the first catalysts tested for glucose isomerisation into fructose, following the conventional Lobry de Bruyn–Alberda van Ekenstein mechanism [13]. Hydrotalcites, alkaline-exchanged and MgO-impregnated zeolites, anion-exchanged resins, mesoporous ordered molecular sieves of the M41S family, magnesium oxide and metallosilicate solid bases are among the already published materials [18–27]. The successful application of materials containing Lewis acid sites for the glucose isomerisation into fructose was more recently discovered, with Ti- and Sn-promoted zeolites and mesoporous silicas being the most studied solids [28–30].

Both basic and Lewis acid zeolites have been shown to be attractive

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catalysts for glucose isomerisation into fructose at mild operating conditions. However, reduction of textural properties as a result of the addition of activity promoters has been one of the reported drawbacks. In fact, in our earlier work, the incorporation by impregnation of increasing amounts of magnesium oxide (up to 15 wt.%) to a NaY zeolite with the purpose of boosting the catalyst activity was observed to negatively affect fructose selectivity [27]. This was ascribed to a partial porosity blockage due to magnesium addition that increases fructose residence time inside the zeolite structure and so promotes its further transformation. References to limitations in the use of some zeolite structures due to their small pore size are commonly found in the literature, when using Ti- and Sn-containing zeolites [28–30]. It has been claimed that intermediate pore zeolites, such as the MFI, have only a residual activity when compared to BEA zeolites, as glucose molecules are too voluminous to diffuse along the narrow channels and access the active sites. However, if part of these active sites becomes accessible, activity can be greatly improved, as demonstrated by Li et al. [30] when studying Sn-zeolites by DFT. Sn-MWW and Sn-MFI are zeolites with similar pore size, but Sn-MWW is much more active than the Sn-MFI as intrazeolitic Sn sites are slightly more accessible in the MWW structure.

Diffusion inside zeolites can be significantly enhanced by generating mesoporosity into the structure through post-synthesis procedures. Desilication has been verified to be a very suitable method of obtaining combined micro- and mesoporous zeolites with preserved structural integrity [31]. This alkaline treatment allows a selective extraction of silicon from the framework such that framework aluminium is mostly maintained, the extent of Si and Al removal depending on the Si/Al ratio of the zeolite [31–33]. Moreover, mesoporosity is improved without greatly compromising the microporosity of the zeolite [34,35]. Therefore, these hierarchical zeolites have shorter micropore diffusion paths and enhanced access to micropores through the newly created mesopores [31], which can have a beneficial impact on the catalytic activity.

Hierarchical zeolites have not been extensively applied to glucose isomerisation into fructose, but the few existing studies have revealed a very positive influence of their use on both glucose conversion and fructose production [36–38]. The performances of a self-pillared, micro- and mesoporous Sn-MFI zeolite and a regular Sn-BEA zeolite were compared by Ren et al. [36]. For the same level of glucose conversion (85%), a much higher fructose yield was obtained with the hierarchical Sn-MFI zeolite (65 against around 35%). Alkali-treated Sn-MFI zeolites were also tested for the reaction [37]. No activity was found for the parent Sn-MFI zeolite, but glucose conversions between 13–21 and 35–41% could be achieved after 15 min and 2 h over the alkali-treated Sn-MFI zeolites. Fructose yields were also observed to gradually increase with the improvement of the mesoporous surface area. The effect of the desilication of a Sn-BEA was also simulated through DFT calculations [38]. It was noticed that the creation of additional silanol groups by the treatment can enhance the catalytic properties of the SnOH defect sites, as it increases the Lewis acidity of the active centres.

In the present work, hierarchical micro- and mesoporous NaY zeolites impregnated with 5 wt.% of magnesium have been investigated for glucose isomerisation into fructose for the first time. The purpose was to establish the effect of zeolite desilication on the catalytic performance for glucose isomerisation. Low to moderate-severity NaOH alkaline treatments were applied to the NaY zeolite, in order to achieve only a limited degree of desilication. By generating a controlled mesoporosity on the NaY zeolite, it was expected to overcome to some extent the loss of textural properties resulting from magnesium incorporation, improve molecular diffusion, and as consequence enhance glucose conversion and fructose yield. Characterisation of the alkali-treated NaY samples with or without magnesium has been performed by a combination of several techniques, including inductively coupled plasma optical emission spectroscopy (ICP-OES) for elemental analysis, X-Ray diffraction (XRD), N_2 adsorption, pyridine adsorption followed by Fourier transformed infrared (FTIR) spectroscopy, diffuse reflectance ultraviolet-visible (UV–vis) spectroscopy, solid state ^{27}Al and ^{29}Si magic-angle spinning (MAS) nuclear magnetic resonance (NMR), thermogravimetry and differential scanning calorimetry (TGA-DSC) and temperature programmed desorption of CO_2 (CO_2-TPD), in order to understand the impact of desilication on activity and selectivity. The effect of desilication on the deactivation trend and the possibility of regeneration of the catalysts are also studied. Overall, it is shown that low-severity desilicated NaY zeolites lead to improved activity and fructose productivity, and they are demonstrated to have the best regeneration capacity among the other desilicated zeolites.

2. Experimental

2.1. Catalyst preparation

The parent NaY zeolite was supplied by Zeolyst (CBV 100), with a global Si/Al ratio of about 2.73 given by elemental analysis. Alkali-treated samples were prepared through treatment of the parent NaY zeolite with aqueous sodium hydroxide (NaOH) solutions, at different concentrations (0.01-0.2 M) using a solution/zeolite ratio of 33 mL/g. After heating the NaOH solution up to 60 °C in a polyethylene bottle equipped with a reflux condenser, the parent sample was added and the mixture was kept at this temperature under stirring for 30 min. After the alkaline treatment, the zeolite suspension was immediately cooled down with an ice bath and filtered. The liquid filtrate was recovered and the extracted quantities of Si and Al were determined by inductively coupled plasma (ICP). Afterwards, the zeolite was washed with deionised water until neutral pH and dried overnight in the oven at 100 °C. In order to make sure that the alkali-treated zeolites were fully exchanged with Na, three consecutive ion-exchanges were carried out using a 2 M $NaNO_3$ aqueous solution at 25 °C for 4 h with a solution/zeolite ratio of 4 mL/g. After the ion-exchanges, samples were washed with deionised water, filtered, dried overnight in the oven at 100 °C and finally calcined at 500 °C under air flow. Na-exchanged alkali-treated zeolites were identified as $NaY_{concentration}$, where concentration refers to the NaOH solution concentration used for the treatment.

5 wt.% of magnesium was then incorporated on the parent and alkali-treated zeolites by incipient wetness impregnation, using magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$, Sigma-Aldrich, 99% purity) as precursor salt. An aqueous solution of the Mg salt with a water volume close to that of the zeolite pores was added drop-wise to the zeolite, while stirring. After that, samples were once again dried in an oven overnight at 100 °C and calcined at 500 °C under air flow. After magnesium impregnation, the parent zeolite was designated as 5% MgNaY and the alkali-treated samples as $5\%MgNaY_{concentration}$, where concentration refers to the NaOH solution concentration used for the treatment.

2.2. Catalyst characterisation

Si, Al, Na and Mg contents on the zeolites were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Varian Vista MPX ICP-OES system.

XRD patterns were obtained in a PANalytical X'Pert Pro diffractometer, using Cu Kα radiation and operating at 40 kV and 40 mA. The scanning range was set from 5° to 80° (2θ), with a step size of 0.033° and step time of 20s. Crystallinity of the samples was calculated from the XRD data by dividing the integrated areas in the 15–35° range for each zeolite and an appropriate reference.

N_2 adsorption measurements were carried out at −196 °C on a Micrometrics 3Flex apparatus. Before adsorption, fresh zeolite samples were degassed under vacuum at 90 °C for 1 h and then at 350 °C overnight. Spent samples were degassed at 120 °C for 1 h. The total pore volume (V_{total}) was calculated from the adsorbed volume of