Separation of 2,3-Butanediol Using ZSM-5 Zeolite Modified with Hydrophobic Molecular Spaces

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Zeolite modified with the hydrophobic molecular spaces is presented here for separating 2,3-butanediol (2,3-BDO). The space layer favors the passage of organic alcohols through it and their storage in it. Combined with selective ether desorption, this efficiency-improved strategy could be an alternative route for obtaining the high-quality 2,3-BDO.

The imminent energy crisis is a global concern. Renewable resources are thus required urgently. Extensive researches have been launched on both biomass conversion and the subsequent separation procedures. Bio-ethanol or relevant bio-based chemicals are famous alternative renewable sources, which have been widely used to partly replace fossil fuels and other chemicals in the fields of modern industry and transportation. However, the low concentration of organic production obtained from fermentation broth strongly influences the productivity and even affects the economic viability. Therefore, separation of this part of useful production is crucial because of the inherent limitation of microorganisms and the related biorefinery techniques.

2,3-Butanediol (2,3-BDO) is one of the most important biofuels and organic chemicals[1] with broad applications such as a fuel additive, an antifreeze agent, perfumes, a flavoring agent, and a carrier for pharmaceuticals.[1–4] Recently, we successfully developed a new biosynthetic route to obtain 2,3-BDO, which presented a superior optical activity because (*R,R*)-2,3-BDO is obtained with fewer by-products.[5] Therefore, their effective separation is desirable. However, conventional methods such as pervaporation[6] and steam stripping[7] are not very suitable, because high temperature is required that may influence the optical activity. Other methods, including solvent extraction,[8–13] salting out,[14] reverse osmosis,[2] and in situ recovery,[15] usually lead to unwanted higher energy consumption. Nevertheless, an adsorption–desorption model is available for obtaining a more optically active product compared to those obtained using above-mentioned methods, because room temperature or lower temperature is employed. Hydrophobic zeolites are promising absorbents, which have been intensively studied for investigating bio-ethanol adsorption and recovery based on the hydrophobicity of the zeolite derived using its Si/Al ratio. However, fewer efforts were made to adsorb 2,3-BDO, probably because of the larger molecular volume than that of ethanol. With these considerations, we developed a strategy by utilizing the hydrophobic surface modification on the zeolite surface, other than modulating its Si/Al ratio. The modified hydrophobic molecules will further act as space layer[16–18] on the solid–liquid interface, which favored the passage of BDO through it and its storage there. An efficiency-improved result is realized when the above-mentioned process was combined with the subsequently designed ether-desorption process. Thus, this strategy may be an alternative route for BDO separation in practical applications.
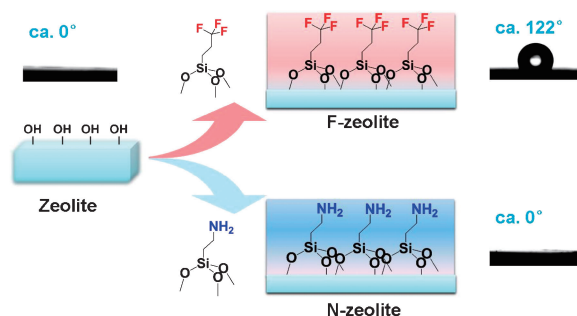
Scheme 1. Schematic representation for the surface-modification of the ZSM-5 zeolite. The insert pictures exhibit the actual wettability studies. The zeolite samples modified with the trifluorosilane and the aminosilane were denoted as F-zeolite and N-zeolite, respectively.

It is well known that ZSM-5 zeolite has an MFI framework with zig-zag channels, with a diameter of ca. 0.5 nm, running in both the *a* direction and *b* direction.[19] Scientists have explored that the intrinsic Si/Al ratio can influence the adsorption properties by improving the external hydrophobicity of the zeolite;[20,21] thus, highly hydrophobic zeolites are usually employed. By further considering the space layer on the interface from such a wettability point of view, we created the surface hydrophobicity of the ZSM-5 zeolite by using a surface-modification method with trimethoxy(3,3,3-trifluoropropyl)-silane. As schematically shown in Scheme 1, the trifluorosilane was easily assembled onto the zeolite surface with two-step procedures (see Supporting Information (SI) for details):[22–24] briefly, first obtain surface hydroxy groups using alkali, and then immerse the dried powder in an anhydrous trifluorosilane solution. This leads to the fabrication of an enhanced hydrophobic space layer. On the one hand, we predict that the extrinsic hydrophobic modification will improve the absorptive power; on the other hand, we believe that the molecule layer of trifluorosilane will create additional interspaces that act as reservoirs for lipophilic molecules, for example, 2,3-BDO used in this work, thus advancing the efficiency of both the process of sorption and the state of being sorbed. For comparison purpose, studies on a naked ZSM-5 zeolite and a hydrophilic space layer of 3-aminopropyltrimethoxysilane were also carried out (Scheme 1).

Scheme 1 also shows the actual results on wettability (inset pictures) for the naked and surface-modified ZSM-5 zeolite. The naked ZSM-5 zeolite surface showed wettability with a contact angle (CA) of 0° on the pressed powder pellet, mainly due to the surface roughness. After modifying with trifluorosilane, the zeolite surface became more hydrophobic with a macroscopical CA of approximately 122°. Otherwise, using the same procedure for the sample modified with aminosilane, the surface wettability
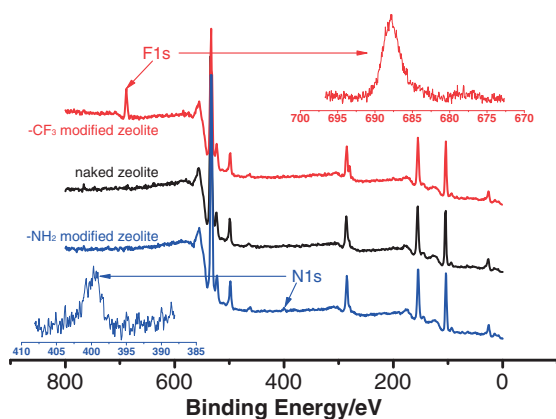
Figure 1. XPS measurements of the naked and modified zeolite samples. The insert spectra are obtained from the F1s and N1s regions, respectively.

Figure 2. Analytical results of the absorbed masses in the naked and modified zeolites. The zeolite samples modified with the trifluorosilane and the aminosilane were denoted as F-zeolite and N-zeolite, respectively.

exhibited a superhydrophilic CA of 0°. It thus proved that the zeolite surface covered with a layer of hydrophobic molecules as the external space has the ability to modulate surface wettability.

The modified molecular spaces were further confirmed by the X-ray photoelectron spectroscopy (XPS), as shown in Figure 1. In this study, we focused particularly on CF_3-terminated and NH_2-terminated groups, because these F and N elements are not initially present in the ZSM-5 zeolite. The datum line was characterized by the naked zeolite, and no F1s or N1s signal was detectable (black line in Figure 1). In contrast, in Figure 1, a sharp F1s signal peak at 687.9 eV was detected on the trifluorosilane-modified zeolite, and a distinct N1s signal was observed in the 399.5 eV region for the sample containing the aminosilane component.[25] This clearly demonstrates that the coating molecules had indisputably assembled onto the zeolite surface.

However, because it was difficult to selectively characterize the actual surface properties of the individual zeolite micropowders before and after the silane treatment using the above methods, as a model unit in the following separation procedures, we measured the powders by using a scanning electron microscope (SEM). The SEM images (Figure S1)[24] exhibited a dispersive character of the zeolite powders without any congeries before and after silane modification. Furthermore, porosity detections were carried out to demonstrate that pore blocking does not occur after silane modification and that the functional groups are dominantly attached on the outer surface of zeolite particles. The results of Horvath–Kawazoe cumulative pore volume plot (the original HK method) are showed in Figure S2.[24] The summary reported that the maximum pore volume and the median pore width are, respectively, 0.1151 $cm^3 g^{-1}$ and 0.4415 nm for naked zeolite, 0.0997 $cm^3 g^{-1}$ and 0.4489 nm for F-zeolite, and 0.0925 $cm^3 g^{-1}$ and 0.4442 nm for N-zeolite. Combining the above-mentioned analyses, it can be concluded that the treatment procedures were coincident with our expectation for surface modification.

After modifying the interfacial space, we performed the adsorption experiments using three types of zeolites. First, a conventional adsorption–desorption method was carried out. The typical process is described here briefly. Herein, 3 g of the given
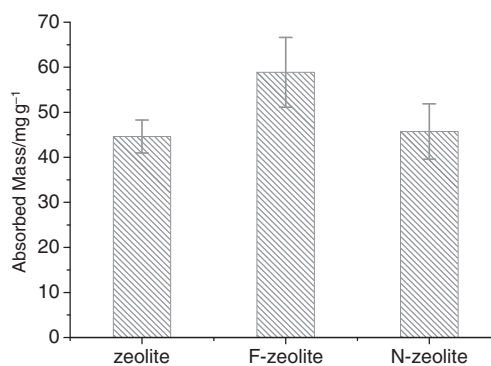
zeolite was immersed into 30 mL of rough-wrought fermentation broth, which mainly contained 287 mg of BDO and 238 mg of glycerol; the crude glycerol was used as a raw material in the fermentation. The powders were kept in the broth for 4 h under soft stirring to achieve the adsorption equilibrium. Then, the zeolite was separated from the broth and dispersed in ethanol to preform desorption. The organic phase was separated, dried with anhydrous sodium sulfate, and finally evaporated to obtain the product. The component was analyzed by high-performance liquid chromatography (HPLC). The analytic data are displayed in Figure 2.

From Figure 2, by comparing with the naked zeolite powders (44.6 ± 2.6 mg g^{-1}), a distinct improvement could be found for the F-zeolite (58.9 ± 5.8 mg g^{-1}). For the efficacy, an increase of ca. 33% was given in the statistics, which was mainly contributed by the hydrophobic interfacial layer. In our viewpoint, the CF_3-modified layer not only supplied a surface hydrophobic property but also constructed a molecular space at the interface between water and zeolite; thus, it would prevent water from entering the zeolite channel while the interface favored the free passage of organic alcohols in the adsorption process. On the other hand, the NH_2-modified layer did not show any valuable promotion (45.7 ± 4.9 mg g^{-1}), because the hydrophilic molecular space of N-zeolite could not prevent water from contacting the zeolite surface. This comparable data confirmed our deduction in some aspects.

However, the HPLC analysis detected nonignorable signals of glycerol with a ratio of 14.8% in the adsorbed organic matters (Figure 3b). Though this is much lower than the ratio of the initial fermentation broth (42.9% in Figure 3a), it is still too higher for obtaining the high-quality BDO. Because glycerol is the inherent component of fermentation (68.0% is the theoretical maximum for the conversion rate),[5] the formation of raffinate and its further adsorption are inevitable. Therefore, we optimized the desorption process by using diethyl ether as the elution solvent instead of ethanol because diethyl ether has good solvency to BDO while glycerol is almost insoluble in it. After performing the same desorption procedures with diethyl ether, only 1.5% of glycerol is detected in the desorbed solution, and the purity of BDO is greatly improved to 97.8%, as shown in Figure 3c. It thus confirmed that diethyl ether is more suitable than ethanol for BDO desorption.
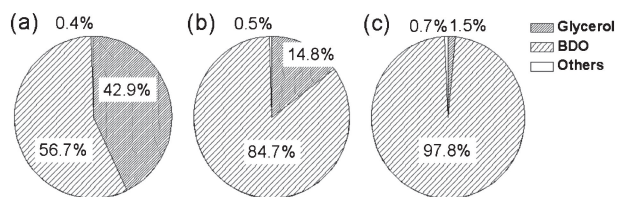
Figure 3. HPLC analyses of BDO and glycerol for the rough-wrought fermentation broth (a), and the produce desorbed by ethanol (b) and ether (c) from F-zeolite.
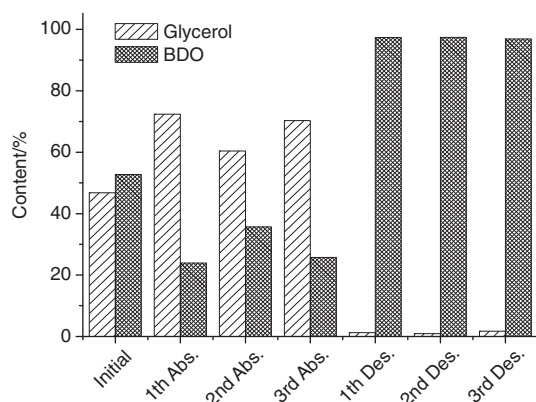

Figure 4. The typical experimental results for 3 cycles of the adsorption (short as Abs.) and desorption (short as Des.) processes.

To further improve the efficacy of the BDO separation, we optimized the separating process by adopting a centrifugal procedure. Because when the zeolites undergo filtration via the conventional method, the liquid will continuously pass through the interfacial space. The washing force combined with the solvent polarity is disadvantageous for the adsorbed organic mass. However, during centrifugation, the solid powders enrich and separate from the liquid, where the hydrophobic units get together and form a hydrophobic interface between the aqueous and solid phases; thus, the interface faces lesser external force. In particular, this centrifugal method can be carried out in the industry by utilizing centrifugal separator sequentially in the adsorption and desorption processes.

On the basis of the analysis described above, we performed the cyclic test for this system. Figure 4 shows the results of three cycles of experiments. After the first adsorption process, the concentration of glycerol increased to 72.4% from the original 46.8%, while the product concentration of BDO decreased to 23.9% from the fresh 52.7%. In contrast, the desorption data showed a clear BDO content of average 97.0% and a glycerol ratio of 1.5%. Though this cyclic performance could not extract all the BDO from the mixture, the above procedures may supply a potential route to realize a dual-circulation (see SI for the brief flowchart)[24] in practical applications. The modified zeolite could draw out BDO product in the adsorption process, and the adsorbed BDO will be separated by ether with higher purity in the desorption process. Nevertheless, ether restrict the separation of glycerol; thus, the concentrated filtrate containing higher concentration of glycerol (ca. 72%) could be cycled to the initial part for refermentation.

In summary, zeolite modified with the trifluorosilane space would prevent water from approaching the zeolite channel while the interface favors the passage of organic alcohols during the adsorption process. In particular, this type of molecular space is more like a functional layer to further hold the organic molecules because they extend the interspaces from the zeolite surface to the terminal trifluoromethyl groups. Thus, we deduced that the modified molecular spaces contribute two advantages in the adsorption process: one is increasing the hydrophobicity of the interface, and the other is extending the space for the adsorbed larger organic molecules; for example, BDO in this study. This study gives us a new insight on surface modification and suggest that the improvement might be an alternative route in biorefinery.

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