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With Open Arms: Open Sites of ZrBEA Zeolite Facilitate Selective Synthesis of Butadiene from Ethanol

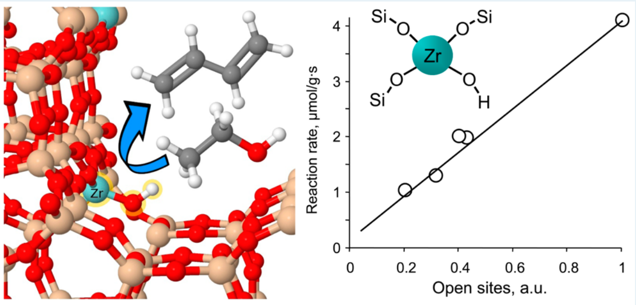
Vitaly L. Sushkevich,[†] Dennis Palagin,[‡] and Irina I. Ivanova*,[†]

[†]Department of Chemistry, Lomonosov Moscow State University, 119991, Leninskye Gory 1, bld. 3, Moscow, Russia

[‡]Physical and Theoretical Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford, OX1 3QZ, United Kingdom

S *Supporting Information*

ABSTRACT: Fourier transform infrared spectroscopy and density functional theory calculations have been used to elucidate the nature of active sites of ZrBEA zeolite responsible for the catalytic synthesis of butadiene. We show that the content of open Zr(IV) Lewis acid sites, represented by isolated Zr atoms in tetrahedral positions of the zeolite crystalline structure connected to three −O−Si linkages and one OH group, correlates with the catalytic activity in the process of conversion of ethanol into butadiene. The higher catalytic activity of the open sites is attributed to their higher acid strength and steric accessibility. The study suggests that the control of such open sites plays a crucial role for the further design of the optimal multifunctional zeolite-based catalysts.



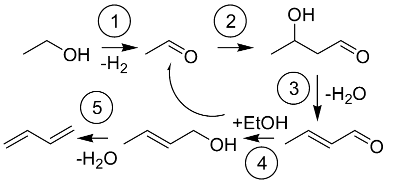
KEYWORDS: *Zr-beta, zeolite, open sites, DFT, FTIR*

Zeolite-based materials constitute an important new class of solid catalysts that attract attention due to their well-defined active sites exhibiting high activity in a wide variety of important reactions.[1] The discovery of SnBEA zeolite as a catalyst for a range of reactions was an important breakthrough in the use of Lewis acids as heterogeneous catalysts.[2] A more recent example is a ZrBEA, which contains Zr(IV) sites introduced in the β-zeolite framework.[3] The uniform distribution of isolated Zr Lewis acid sites, in combination with the unique porous structure of the material, results in an unrivaled catalytic performance in a number of industrially important processes,[4−10] including the synthesis of butadiene from ethanol.[8]

The latter reaction is very important for the diversification of the industrial routes of synthesis of butadiene, which is an important monomer for the production of rubbers and elastomers. Isolation of butadiene from naphtha steam cracker fractions of paraffinic hydrocarbons is the major production route,[11] which however lacks efficiency, especially in an environmental perspective.[11,12] The alternative ethanol conversion process is a promising sustainable substitute for the dominant naphtha-based method, capable of contributing to the decrease in use of fossil fuel reserves, which stimulated a new wave of research over the past five years.[13−21]

Recent developments render the ZrBEA zeolite as a material with very high potential as a catalyst for the conversion of ethanol into butadiene.[8] However, the nature of ZrBEA active sites, which is a necessary prerequisite for understanding mechanisms of reactions and design of new catalysts, has not been fully understood. The kinetic studies performed over Zr-containing catalysts[8,17] has revealed that of the five reaction steps that constitute the target reaction pathway leading to butadiene (Chart 1), steps 1, 2, and 4—namely, ethanol dehydrogenation, acetaldehyde condensation and Meerwein−Ponndorf−Verley−Oppenauer (MPVO) reduction of crotonaldehyde with ethanol—are the key reaction steps.[15] Addition of metal promoter, such as silver, copper, or nickel,[16,17] accelerates the ethanol dehydrogenation step, rendering acetaldehyde condensation and MPVO steps rate-limiting.[8,17]

Chart 1. Main Reaction Pathway of Ethanol to Butadiene Conversion



The investigation of the latter steps over Zr-containing catalysts suggested that both reactions are governed by the Lewis acidity,[7,22] with the overall activity of the metal-promoted Zr-based molecular sieves correlated with Lewis acidity of the

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catalyst. Recent studies based on the FTIR spectroscopy have allowed identification of two distinct types of Lewis sites, designated as closed and open Zr(IV) sites[23] in analogy with the data obtained for the SnBEA zeolite[24] (Chart 2). However, the real configuration of the present sites, as well as their corresponding catalytic activity, remains unknown.

Chart 2. Configurations of Closed (left) and Open (right) Sites of the ZrBEA Zeolite

These challenges motivate the present study of the nature of the active sites of the ZrBEA zeolite. ZrBEA zeolites with a Si/Zr molar ratio within 100−800 promoted with silver were tested for the ethanol conversion into butadiene and showed excellent catalytic activity in terms of butadiene yield and selectivity. Combining spectroscopic and computational chemistry approaches along with the studies of reaction kinetics, we show that the open Zr(IV) Lewis acid sites are mainly responsible for the catalytic activity of ZrBEA in the conversion of ethanol to butadiene and suggest that the control over the number of such sites by varying the Zr loading and distribution is the key for a rational design of novel multifunctional zeolite-based catalysts.

To study the nature of active Zr sites, a series of ZrBEA catalysts with different Si/Zr ratios was prepared. The samples are designated thereafter as ZrBEA(*x*), where *x* is a Si/Zr ratio. All materials were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), ^{29}Si magic-angle spinning nuclear magnetic resonance (^{29}Si MAS NMR), nitrogen adsorption−desorption, and elemental analysis. The data are summarized in the Supporting Information.

For the catalytic tests, ZrBEA materials were doped with 1 wt % of silver to promote a dehydrogenation reaction to convert ethanol into acetaldehyde. The content of the silver promoter was optimized previously[8,17,25] to accelerate the rate of the dehydrogenation step (step 1, Chart 1) with respect to condensation and MPVO (steps 2,4 Chart 1) and to ensure that the overall reaction rate is controlled by the Lewis acid sites. The examination of the silver distribution and particle size by TEM and SEM/EDX (Figures S5, S6) shows a uniform distribution of silver particles of 2−5 nm on the surface of the ZrBEA, which is required for ethanol dehydrogenation.[25]

The conversion of ethanol into butadiene over ZrBEA promoted with silver catalysts was studied at 593 K, atmospheric pressure, and weight hour space velocity within 0.1−0.6 h^{-1}. These reaction conditions were found to be optimal for the selective synthesis of butadiene over Zr-containing catalysts.[17]

The results of the catalytic activity tests presented in Table 1 show that the increase in the Zr content in ZrBEA from 20 to 122 μmol/g leads to significant enhancement of the initial rates of the reaction from 0.72 to 2.64 μmol/g·s; however, no direct correlation is observed. Thus, for the samples of ZrBEA(260) and ZrBEA(460) ethanol, conversion rates are almost identical, whereas the Zr content differs by a factor of 2.

Such behavior of ZrBEA catalysts suggests that Lewis sites generated by the incorporation of Zr atoms into the zeolite framework are not equal in catalytic activity. In particular, open and closed Zr sites may possess different activities in the reaction, and their content may be strongly influenced by the Si/Zr ratio in the zeolite.

Table 1. Catalytic Properties of ZrBEA Samples in Ethanol Conversion into Butadiene

catalyst	Zr content, μmol/g	initial rate, μmol/g·s	butadiene selectivity, mol %
Ag/ZrBEA(130)	122	2.64	64
Ag/ZrBEA(260)	63	1.30	65
Ag/ZrBEA(460)	36	1.34	66
Ag/ZrBEA(610)	27	0.90	68
Ag/ZrBEA(850)	20	0.72	68

The product distribution is shown in Table S2. The results suggest that butadiene is the main reaction product over all the catalysts studied. The main side reactions involve ethanol dehydration into ethylene and diethyl ether; ethyl acetate formation via Tischenko reaction of the acetaldehyde; and unselective reduction of crotyl alcohol, leading to 1-butanol, which dehydration gives a mixture of butenes.[8]

The comparison of the selectivity toward butadiene over different catalysts at the same conversion level of 30% reveals that the selectivity slightly decreases with increasing Zr content. This observation can be due to a higher density of the active sites, which provides for the higher contribution of condensation reactions and therefore a higher amount of heavy byproducts (Table S2). Selectivity toward other side products does not change from Ag/ZrBEA(130) to Ag/ZrBEA(850).

The catalytic activity of Ag/ZrBEA catalysts in the time course of the reaction slightly decreases without changes in product selectivity, indicating gradual poisoning of active sites by coke deposits,[8,17] but the loss of activity during 6 h on stream does not exceed 10%.

To establish the nature of the active sites responsible for the catalytic activity of ZrBEA, samples were studied by FTIR spectroscopy of the adsorbed CO (Figure 1).

This technique was proven to be appropriate to distinguish Lewis sites of different types and to measure their relative amounts.[23] The adsorption of CO at low temperature (~100 K) leads to the formation of H-bonds with OH groups

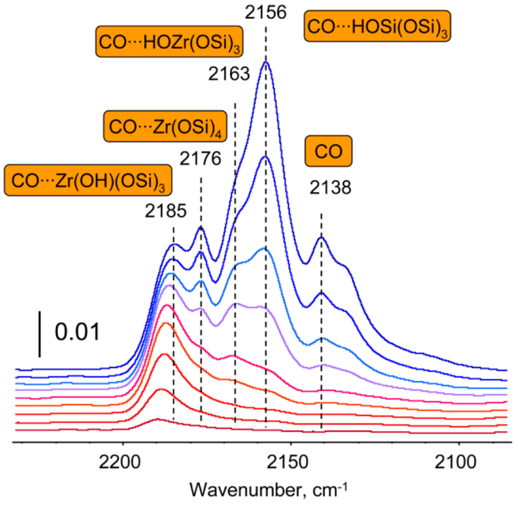

Figure 1. FTIR spectra of CO adsorbed on ZrBEA(130) collected with the increase in the CO coverage. Colored boxes show the configuration of adsorption sites assigned to each peak.

and to the coordination of CO to Lewis acid sites through sigma donation. The vibration band of the adsorbed CO subsequently shifts to higher wavenumbers with respect to the band of pseudoliquid CO (2138 cm^{-1}). This shift is characteristic for the nature and strength of the site.

Calibrated aliquots of carbon monoxide were gradually introduced into the cell cooled with liquid nitrogen, and the IR spectra were subsequently recorded (Figure 1). With increase in CO pressure, the bands at 2185, 2163, 2156, 2176, and 2138 cm^{-1} were successively observed in spectra.

In accordance with ref 23, the high-frequency bands (2185 and 2176 cm^{-1}) were attributed to the CO adsorption on the Lewis sites, whereas the low frequency bands (2163 and 2156 cm^{-1}) were assigned to the CO interacting with OH groups. The last band observed at 2138 cm^{-1} was due to pseudoliquid CO vibrations. The actual configuration of the sites detected was further verified by DFT calculations, which have been carried out using four cluster models, corresponding to the adsorption of CO molecule on metal centers of the closed and open sites of the ZrBEA as well as on the OH groups of the Zr- and Si-centered open sites (Figure 2). The structures obtained by adsorption of CO on the proposed cluster models were optimized within the DFT framework at the hybrid functional level. Vibrational spectra have been calculated within the harmonic approximation.

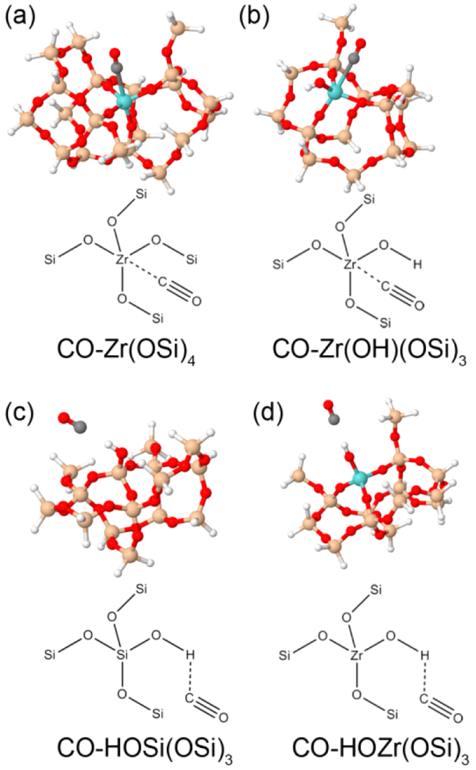

Figure 2. DFT-optimized structures of CO adsorbed on closed (a) and open (b) sites of ZrBEA as well as on OH groups of (c) Si- and (d) Zr-centered open sites. Atomic coordinates of each structure are available in the Supporting Information.

Calculated vibrational frequencies of the adsorbed C−O group allowed unambiguous identification of the four experimentally observed bands. Two lower-frequency bands belong to the CO adsorption on the OH groups: the CO−HOSi(OSi)$_3$ complex yields 2158 cm^{-1} vibration, and the CO−HOZr(OSi)$_3$ is featured at 2165 cm^{-1}. These results are in good agreement with experimental values of 2156 and 2163 cm^{-1}, respectively. Two higher vibrational frequencies are due to CO interaction with Zr atoms of the closed (CO−Zr(OSi)$_4$, 2177 cm^{-1}) and open (CO−Zr(OSi)$_3$OH, 2181 cm^{-1}) sites of the ZrBEA. The calculated values are very close to the experimentally obtained ones (2176 and 2185 cm^{-1}, respectively). Physisorbed CO (simulated by adsorbing a second CO molecule to an already "occupied" adsorption site) yields the C−O vibrational frequency of 2137 cm^{-1}, which agrees well with the experimentally measured value of 2138 cm^{-1} of pseudoliquid CO.

Calculated adsorption energies support the above assignment of the IR bands. In the case of direct adsorption of the CO molecule on the metal center, the adsorption energy is ~1.7 kcal/mol higher than in the case of the interaction with the OH group, which agrees well with the higher vibrational frequencies observed in experiment.

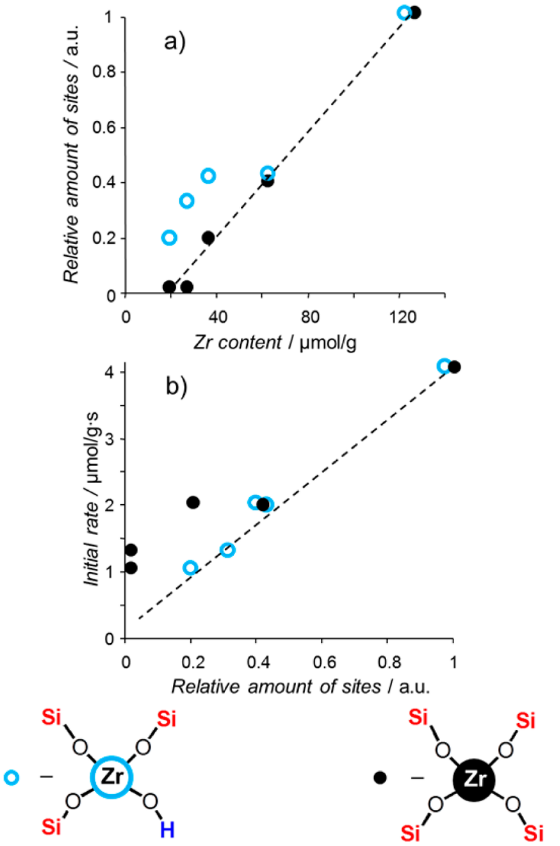

Figure 3. Relative amount of open and closed Lewis sites determined by FTIR spectroscopy of adsorbed CO versus Zr content (a) in silver-promoted ZrBEA samples and (b) versus initial rates of ethanol conversion.

In further experiments, ZrBEA catalysts with different Zr loadings were compared, and similar set of bands were observed for all samples (Figures S7, S8). The normalized intensities of the bands at 2185 (open sites) and 2176 cm^{-1} (closed sites) were plotted versus the Zr content in the samples as shown in Figure 3a.

The results indicate that the relative amount of closed sites is linearly correlated with Zr content. The band corresponding to open sites has different behavior: at low Zr contents, the relative number of open sites decreases much more slowly than the number of closed sites. Thus, ZrBEA(260) and ZrBEA(460) show nearly the same numbers of open sites, as noted above.

The comparison of the results obtained over different ZrBEA catalysts in ethanol conversion into butadiene with the results of infrared spectroscopy of adsorbed CO points to a linear correlation between the catalyst activity and the relative content of the open sites (Figure 3b). The number of closed sites, on the other hand, does not show a direct correlation with activity. All these observations suggest that the activity of the ZrBEA catalyst depends on the content of open Zr(IV) Lewis sites, whereas closed Zr(IV) sites seem to be inactive or less active in this reaction. The higher activity of the open sites could be attributed to their high acid strength as well as to better steric accessibility compared with the closed sites.

In summary, we have systematically studied the nature of the activity of Ag/ZrBEA zeolite catalysts in the reaction of the conversion of ethanol into butadiene. Our results suggest that the Zr(IV) Lewis acid sites in such a catalyst are represented by isolated Zr atoms in the tetrahedral positions of the zeolite crystalline structure linked with four (closed site) and three (open site) silicon atoms. Combining the results of Fourier transform infrared spectroscopy and density functional theory calculations revealed that the open sites of ZrBEA are the most efficient in the reaction of butadiene synthesis, which can be rationalized in terms of higher acid strength and better steric accessibility of such sites. Our study suggests that by varying the amount of Zr, it is possible to control the number of open sites and, thus, the catalytic activity of the ZrBEA zeolite. These findings illustrate the diversity and flexibility available to zeolites as catalytic materials due to the tunability of their properties via adjusting the nature and the number of their adsorption sites and facilitate further design of the optimal multifunctional catalysts.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b01024.

> Detailed synthetic procedures and characterization, nitrogen adsorption−desorption isotherms, XRD, XPS, ^{29}Si MAS NMR, additional FTIR spectra, (by)-products distribution for all Ag promoted ZrBEA catalysts, and details of the DFT calculations together with atomic coordinates of all discussed structures (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: iiivanova@phys.chem.msu.ru.

Notes

The authors declare no competing financial interest.

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