Methane activation by Zn-modified zeolites: solid-state NMR and DRIFTS investigation of the performance of Zn\(^{2+}\) and ZnO sites

Anton Gabrienko,\(^{a,b,*}\) Sergei Arzumanov,\(^{a,b}\) Dieter Freude,\(^{c}\) Alexander Stepanov\(^{a,b}\)

\(^{a}\)Novosibirsk State University, Novosibirsk, 630090, Russia
\(^{b}\)Boreskov Institute of Catalysis, Novosibirsk, 630090, Russia
\(^{c}\)Universität Leipzig, Leipzig, 04103, Germany

*Corresponding author: +7 (383)330-80-56, gabrienko@catalysis.ru, a.gabrienko@g.nsu.ru

Abstract: This work addresses an important problem of methane conversion at Zn-modified zeolites. The mechanism of methane activation has been meticulously investigated with two advanced methods: solid-state NMR and DRIFTS. Particularly, two different types of possible Zn-sites, isolated Zn\(^{2+}\) cations and small ZnO clusters located inside of zeolite channels, have been compared with respect to their ability to activate and convert methane. The kinetics of both H/D exchange of methane-\(^{d}\)\(_4\) with zeolite Brønsted acid sites and surface Zn-methyl species formation has been monitored with the solid-state NMR approach \textit{in situ}. DRIFTS has revealed methane specific interactions with Zn-sites.

Keywords: methane activation, Zn-modified zeolites, solid-state NMR, DRIFTS.

1. Introduction

Methane chemical activation is an important challenge since it is a key for methane conversion to valuable compounds, such as aromatics, acetic acid, methanol, etc. High-silica zeolites (ZSM-5, BEA) modified with Zn have demonstrated an ability to activate and convert methane either directly\(^{1-5}\) or jointly with higher hydrocarbons.\(^{6-8}\) To improve catalytic properties of the Zn-containing zeolites, it is important to know which Zn-sites are active and how these sites work during methane transformation on the surface of the zeolites. Despite of the numerous studies, these issues have not been properly understood yet.

In general, there are two options for Zn stabilization when it is loaded into a zeolite: isolated Zn\(^{2+}\) cations or small ZnO clusters located inside zeolite channels. Herein, the performance of these possible Zn-sites with respect to methane activation and conversion has been studied with the help of advanced solid-state NMR and DRIFTS approaches. Specifically, the kinetics of H/D exchange of methane-\(^{d}\)\(_4\) with zeolite Brønsted acid sites and surface Zn-methyl species formation has been monitored with the solid-state NMR approach \textit{in situ}. DRIFTS has revealed methane specific interactions with Zn-sites.

2. Experimental

The zeolite samples, containing isolated Zn\(^{2+}\) cations (Zn\(^{2+}\)/H-BEA, Zn\(^{2+}\)/H-ZSM-5) were prepared by the exposure of pure acid-form zeolites H-BEA or H-ZSM-5 to metallic Zn vapor according to the procedure reported earlier.\(^9\) The sample ZnO/H-BEA, containing exclusively ZnO species, was prepared by multistep synthesis including dimethylzinc hydrolysis inside zeolite pores. The characterization of the synthesized zeolites was performed with EXAFS, XPS, electron microscopy and solid-state NMR with regard to the nature, structure and composition of Zn species, their dimensions and distribution within the zeolite crystals, the quantity of the residual BAS.

NMR experiments were performed using a Bruker Avance-400 spectrometer equipped with a broadband double-resonance MAS probe. An approach of sealed glass ampules was utilized to obtained reliable NMR data. For \(^{13}\)C CP/MAS NMR, the proton high power decoupling field strength was 11.7 G (5.0 \(\mu\)s length of 90° \(^1\)H pulse); contact time was 2 ms at the Hartmann-Hahn matching condition of 50 kHz; and the
delay between scans was 2 s. DRIFTS spectra were recorded on a Shimadzu FTIR-8300 spectrometer equipped with a standard diffuse-reflectance attachment in the range of 400–6000 cm\(^{-1}\), with a resolution of 4 cm\(^{-1}\) and 250 scans for signal accumulation.

3. Results and discussion

In situ \(^1\)H MAS NMR analysis of the kinetics of H/D hydrogen exchange\(^{10}\) between BAS of the zeolites and methane-\(d_4\) has revealed a dramatic increase of the exchange rate by two orders of magnitude for ZnO/H-BEA and by three orders of magnitude for Zn\(^{2+}\)/H-BEA as compared to the parent zeolite H-BEA (Figure 1). Hence, both isolated Zn\(^{2+}\) cations and ZnO clusters located inside zeolite channels exhibit promoting effect on the reaction of the H/D exchange. This can be rationalized in terms of synergistic action of both Zn species and BAS for methane C–H bond activation resulting to noticeable acceleration of the H/D exchange for both zeolite samples.

The performance of different Zn-sites has also been examined with respect to the reaction of benzene alkylation with methane. It has been found that only isolated Zn\(^{2+}\) species provide the alkylation while ZnO clusters seem to be inactive in this case. \(^{13}\)C solid-state NMR has shown that the interaction of methane with Zn\(^{2+}\) results to the formation of Zn-methyl species (detected by the signal at \(-21\) ppm); on the contrary, these species are not formed upon methane interaction with ZnO clusters. Since Zn-methyl species are the key intermediate for the alkylation reaction\(^{5,6}\), it is clear why only Zn\(^{2+}\)-sites demonstrate the ability to convert methane to aromatics via the alklylation of benzene to form toluene and xylenes.

However, the specific interaction of methane has been revealed with DRIFTS approach for both types of Zn-sites. Particularly, the transient molecular complexes, which are characterized by a band at \(2820\) cm\(^{-1}\) from perturbed \(\nu_1\) C–H stretching, have been observed to form upon methane adsorption on the Zn-modified zeolites. This finding has given us an opportunity to propose a new mechanism of methane C–H bond activation by the Zn-sites.

4. Conclusions

The ability of isolated Zn\(^{2+}\)-sites of Zn-modified zeolites to perform activation of methane C–H bond via dissociation followed by the formation of Zn-methyl species has been demonstrated. On the other hand, small zinc oxide clusters located inside zeolite channels are not able to dissociatively adsorb and therefore activate methane for the conversion via the reaction of benzene alkylation. This result is important for further improvement of the properties of Zn-containing zeolites as perspective catalysts of methane utilization.

References