Direct Conversion of Methane to Methanol by Metal-Exchanged Zeolites: The Effects of Zeolite Confinement and Active Site Structure

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ABSTRACT

Metal-exchanged zeolites are known to exhibit catalytic activity in the direct conversion of methane to methanol. In our first study,[1] we investigate the role of zeolite nanopores on the reactivity of $[MO]^+$-MFI zeolites (M = Fe, Co, Ni, Cu) toward methane oxidation by comparing our results to those for the reaction by bare $[MO]^+$ species in gas phase.[2] We found that the confinement of zeolite nanopores destabilizes the adsorption energy of methane and lowers the C–H bond activation energy, suggesting that the catalytic property of zeolites comes from their confinement effects. In our second study, we investigate the oxidation of methane over $[Cu_2(\mu\text{-}O)]^{2+}$ active species in different types of zeolite framework, i.e. AEI, CHA, AFX, and MFI zeolites. We found that the small-pore $[Cu_2(\mu\text{-}O)]^{2+}$-AEI, -CHA, and -AFX zeolites have lower C–H bond activation energies than the medium-pore $[Cu_2(\mu\text{-}O)]^{2+}$-MFI zeolite does, which agrees with the experiments showing that small-pore Cu-zeolites produce more methanol than medium- and large-pore Cu-zeolites.[3] Our molecular orbital analyses show that it is actually the Cu-O-Cu angle of the $Cu_2(\mu\text{-}O)$ active site, not the zeolite confinement, that is responsible for such reduction of reaction barrier. This suggests that small- and medium-pore zeolites have similar confinement effects. In our third study, we confirm those suggestions by investigating the oxidation of methane over $[FeO]^{2+}$ active species in AEI and MFI zeolites. We found that the similar structures of mononuclear iron-oxo in different types of zeolite framework result in similar C–H bond activation energies.

References:

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