356f Light Alkane Dehydrogenation Activity for [Gah]$^{2+}$ Sites Involving Two Framework Aluminum in Ga-Hzsm-5 Catalysts: a Dft Pathway Analysis

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Light alkane aromatization using shape selective MFI based catalysts is an important chemical process. Unfortunately, substantial cracking activity of unmodified HZSM-5 catalyst leads to large amounts of methane and ethane as undesired byproducts reducing the aromatization selectivity. This problem is overcome by incorporating additional dehydrogenation function in the form of extra-framework species like Ga, Zn and Pt. However, there are varying opinions regarding the role of GaH_X species in the alkane dehydrogenation. Using electronic DFT methods, we have studied the catalytic activity of extra-framework [GaH]$^{2+}$ species in the proximity of the two framework Al, and we propose this as a likely model for the most active Ga-related sites for alkane dehydrogenation. We find that the dehydrogenation activation barriers correlate strongly with reducibility of the [GaH]$^{2+}$ site (and hence the Al-Al distance in the dual site model)—consistent with Brønsted-Evans-Polanyi relationships. The optimal Al-Al separation is governed by the interplay between two compensating reaction steps (C-H activation and H-H formation), exemplifying the applicability of the Sabatier principle for a distribution of the Al-pair sites in the zeolite.