Structure and Catalytic Activity of Zeolite-Supported Molybdenum Carbide Nanoparticles for Methane Conversion

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Mo/ZSM-5 is a promising catalyst for non-oxidative methane dehydroaromatization with benzene as the main product. Initial Mo oxide species in ZSM-5 are known to convert to carbide or oxycarbide nanoparticles [1, 2], but the structure of these nanoparticles has not been systematically studied. The current study systematically evaluates the structure and activity of Mo carbide nanoparticles as a function of their size and composition

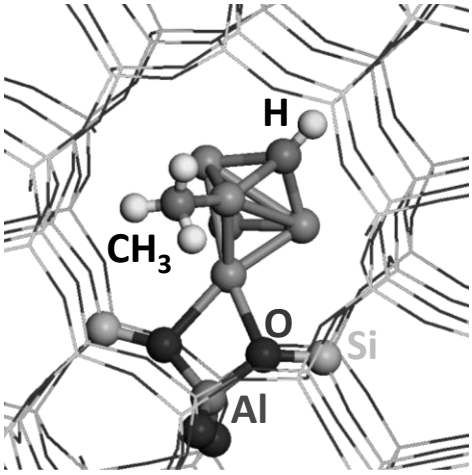

Figure 1: Activated methane on Mo_4C_2 nanoparticle in a ZMS-5 cavity

A mechanism of methane activation over catalytic Mo carbide nanoparticles was developed based on DFT transition state calculations for the first time. In this mechanism, methane is activated by an active site consisting of a neighboring Mo-C pair of surface atoms. The active site splits gas-phase methane by simultaneously stabilizing the CH_3 fragment on a Mo atom and the H atom on a neighboring C atom of the nanoparticle. This reaction mechanism was used to compare the activity of supported Mo_xC_y nanoparticles. The calculations were performed initially using small cluster models for ZSM-5. Subsequent models employed QM/MM calculations using larger clusters for the QM region and a full, periodic unit cell of ZSM-5 for the MM region. Preliminary results indicate that nanoparticles with the stoichiometry Mo_2C (2:1 atomic ratio) have lower activation barriers and, therefore, are expected to be more catalytically active.

1. Ding, W., Li, S., Meitzner, G.D., and Iglesia E., J. Phys. Chem. B 105, 506 (2001).
2. Zheng, H., Ma, D., Bao, X., Jian, Z.H., Ja, H.K., Wang Y., and Peden, C.H.F., J. Am. Chem. Soc. 130, 3722 (2008).