Structure and activity of molybdenum carbide nanoparticles in ZSM-5 for methane conversion to aromatics

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Introduction

Natural gas conversion to liquid fuels and chemical feedstocks is a highly desirable objective. Mo/ZSM-5 is a promising catalyst for non-oxidative methane dehydroaromatization with benzene as the main product. Initial isolated 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 for the first time systematically evaluates the structure and activity of Mo carbide nanoparticles as a function of (1) the nanoparticles size, (2) nanoparticle composition and (3) location of the nanoparticle in the ZSM-5 zeolite framework.

Materials and Methods

Mo/ZSM-5 catalysts with variable Si/Al atomic ratios (15-140) and variable Mo loadings (1-5 wt%) were prepared by incipient wetness impregnation. The catalysts were tested in flow of 1.5 mol% CH_4 in He by simultaneously collecting *operando* Raman spectra and online mass spectra of reaction gases. Gradient-corrected density functional theory (DFT) calculations were performed with the DMol3 code in Materials Studio by Accelrys Software, Inc. The geometry of Mo carbide nanoparticles was first optimized in vacuum and then re-optimized in the ZSM-5 framework. The ZSM-5 structure was modeled with cluster models using DFT and also by clusters embedded into the full periodic ZSM-5 cell using a hybrid quantum mechanics and molecular mechanics method.

Results and Discussion

Evolution of *operando* Raman spectra for 2 wt% Mo/ZSM-5 with Si/Al=15 as a function of time on stream and temperature is shown in Fig. 1. The initial Raman spectrum for Mo oxide on ZSM-5 exhibits bands at ~318, 972 and 997 cm^{-1} assigned to isolated dioxo [$Mo(=O)_2$] species. On CH_4 introduction, these initial Mo species convert to carbide nanoparticles with the formation of CO_2 as the only carbon-containing reaction product. The formed Mo carbides catalyze CH_4 dehydroaromatization with benzene as the main product. At this point in time on stream, CO_2 formation stops, the Raman bands for the initial Mo oxide species are no longer observed and new Raman bands appear at ~1169, 1372, and 1583 cm^{-1} that are characteristic of carbonaceous polyaromatic species on zeolite surfaces.

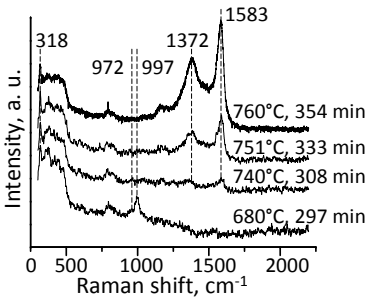

Figure 1. Evolution of Raman spectra for Mo/ZSM-5 in CH_4 flow as a function of temperature and time on stream.

the composition of MoC_xO_y nanoparticles and compare the activity of carbides and oxycarbides. The effect of the carbide nanoparticle size on activity was evaluated by varying the number of Mo atoms from 1 to 12 for several selected compositions. The effect of the nanoparticle location in the zeolite framework was evaluated by comparing the activity of several nanoparticles on a single Al site, on two bridging Al sites and on Si only sites in the pores and on the outer surface. The results indicate that the size and location of Mo carbide nanoparticles do not significantly influence their catalytic activities in methane activation.

The effect of the Mo carbide composition on activity was evaluated computationally by varying the Mo to C ratio from 4 to 0.5. As an example, Mo_4C_x nanoparticles with Mo to C ratios of 2, 1 and 2/3 are shown in Fig. 2. The activity of Mo carbide nanoparticles supported on ZSM-5 was compared using transition state calculations for the first step in methane activation: formation of CH_3 and H on the catalyst surface (Fig. 3). 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. Additional calculations will be performed in order to evaluate the effect of oxygen presence in

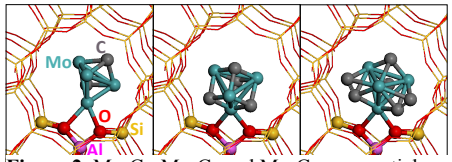

Figure 2. Mo_4C_2, Mo_4C_4 and Mo_4C_6 nanoparticles on a single Al site in the ZSM-5 framework.

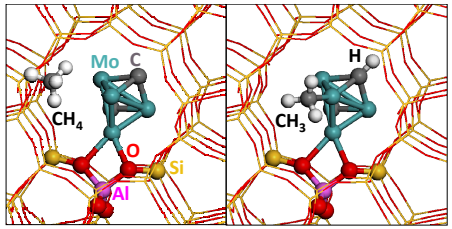

Figure 3. Activation of gas-phase methane over Mo_4C_2 nanoparticle with the formation of CH_3 and H surface species.

Significance

The effects of the composition, size and location in the ZSM-5 zeolite framework for Mo carbide catalytic nanoparticles in methane activation were evaluated for the first time. Nanoparticles with the stoichiometry Mo_2C were identified as being most active. The effects of the nanoparticle size and location were found to be less significant compared to its composition.

References

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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).