

Direct Observation of the Active Center for Methane Dehydroaromatization Using an Ultrahigh Field ^{95}Mo NMR Spectroscopy

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Direct conversion of methane to value-added chemicals remains a challenge from both scientific and industrial points of view. In 1993, Wang et al. reported that methane can be transformed into aromatics on Mo/HZSM-5 catalysts under nonoxidative condition.¹ Although remarkable progress has been made in the studies of the methane dehydroaromatization (MDA) reaction since that time, the reaction mechanism is still being debated,² mainly due to the lack of understanding of the active center on Mo/HZSM-5 catalysts.³ It has been hypothesized that molybdenum may migrate into zeolitic channels and anchor on Brønsted acid sites during the synthesis. However, it is unclear whether the active molybdenum species are small crystallites or isolated exchanged species.

NMR spectroscopy is a powerful tool to study the local electronic structure of observed nuclei. However, the use of solid-state molybdenum NMR is hindered by a combination of the quadrupolar nature of the nucleus ($I = 5/2$), relatively low gyromagnetic ratios (γ), and low natural abundance of the NMR active isotopes.⁴ Therefore, it is not surprising that few studies using solid-state molybdenum NMR have been reported to date.^{5,6} Recently, advancements of “ultrahigh” field NMR spectrometers have made the observation of a wide range of low- γ quadrupolar nuclei feasible.⁶ In this work, a 21.1 T ultrahigh field NMR spectrometer was used for the first time to study the local structure of molybdenum species on Mo/zeolite catalysts. With the significantly improved signal-to-noise ratio at the ultrahigh field, ^{95}Mo NMR spectroscopy is able to recognize different types of molybdenum species on Mo/zeolite catalysts and, by correlating the results with catalytic activity, to reveal the nature of the active center for the MDA reaction.

Mo-based MDA catalysts with four different molybdenum loadings, labeled as xMo/HZSM-5 (x denotes different loadings), were synthesized according to a previously reported procedure.⁷ To improve the sensitivity of NMR spectra, ^{95}Mo -enriched MoO_3 (Cambridge Isotope Laboratories Inc., 94.8% ^{95}Mo) was used as a precursor in the synthesis of these catalysts.

Figure 1 shows the static ^{95}Mo NMR spectra of MoO_3 and the activated catalysts obtained using a standard Hahn Echo sequence, $\pi/2$ - $\tau/2$ - π - $\tau/2$ -acq, where a special phase cycling for quadrupolar nuclei was employed.⁸ The $\pi/2$ pulse width was 2 μs , and the value of τ used was 40 μs . Three break points arising from a combination of the chemical shift anisotropy (CSA) interaction and the electric field gradient (EFG) interaction can be identified from the MoO_3 spectrum with values of approximately -357, -6.0, and 158 ppm, respectively. More accurate NMR parameters can be derived from MQ and MAS NMR experiments.^{6b} The chemical shift reference was 2 M Na_2MoO_4 in D_2O (0 ppm). Compared with MoO_3 , the

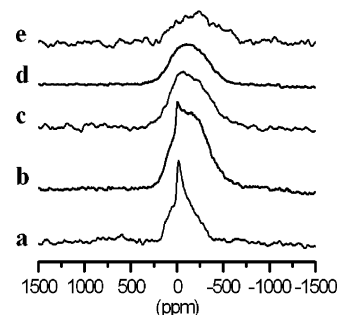


Figure 1. Static ^{95}Mo NMR spectra of **a.** MoO_3 , **b.** 10Mo/HZSM-5, **c.** 6Mo/HZSM-5, **d.** 4Mo/HZSM-5, and **e.** 2Mo/HZSM-5. About 150 mg of samples were used, and each spectrum was acquired using 3000 scans and a recycle delay time of 3 s.

spectrum of 2Mo/HZSM-5 has a much broader peak centered at about -250 ppm, spanning from about -639 to 168 ppm. Apparently, this peak has a quite different line shape and a significant upfield shift relative to the spectrum from MoO_3 . Thus, it can be concluded that the dominant Mo species in the 2Mo/HZSM-5 sample are not the bulk or small crystallites of MoO_3 . Rather a new type of molybdenum species was observed for the first time in these ultrahigh field ^{95}Mo NMR spectra. The spectral line shapes of the samples with higher molybdenum loadings have features that resemble those of MoO_3 , but broader shoulder peaks, centered at about -250 ppm, can also be observed. The chemical shift value of the shoulder peak is the same as that from the new molybdenum species observed in the spectrum from the 2Mo/HZSM-5 catalyst. Therefore, it is reasonable to assign this shoulder peak to the new molybdenum species.

The new molybdenum species may be attributed to the exchanged molybdenum species previously suggested based on ^1H MAS NMR and ^{27}Al MQ MAS NMR results.^{3e,9} Specifically, for the Mo/zeolite system, it has been speculated from the ^1H MAS NMR results that during the impregnation and calcination processes, part of molybdenum species may migrate into zeolitic channels and anchor on Brønsted acid sites, leading to a decrease of the population of these sites.⁹ From an analysis of the ^{27}Al MQ MAS NMR results, it has been inferred that the exchanged molybdenum species may connect with Brønsted aluminum through two oxygen bridges.^{3e} However, there has been no direct evidence via spectroscopy of the molybdenum species itself to support these hypotheses.

Based on ^1H MAS NMR studies, it is known that Brønsted acid sites per zeolitic unit cell in the parent HZSM-5 and the 2Mo/HZSM-5 samples are 3.6 and 2.7, respectively.⁹ The decrease of 0.9 Brønsted acid sites per unit cell in the 2Mo/HZSM-5 sample matches the amount of the new type of molybdenum species (0.92/unit cell) detected by our ^{95}Mo NMR and elemental analysis (see

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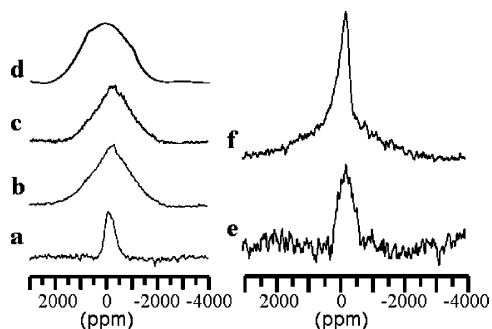


Figure 2. Static ^{95}Mo NMR spectra of **a.** fresh 6Mo/HZSM-5, **b.** 6Mo/HZSM-5 after 15 min reaction, **c.** 6Mo/HZSM-5 after 1 h reaction, **d.** Mo_2C , **e.** fresh 2Mo/HZSM-5, and **f.** 2 Mo/HZSM-5 after 15 min reaction. The experimental conditions were the same as those in Figure 1 except that about 1 g of catalyst was used in cases of (b), (c), and (f).

the Supporting Information). This confirms the previous hypothesis that each molybdenum atom replaces one Brønsted acid site to form the exchanged molybdenum species.^{3c,9} The new type of molybdenum species centered at around -250 ppm can therefore be unambiguously attributed to the exchanged molybdenum species, which dominates the spectrum of the 2Mo/HZSM-5 sample (see Figure S2). For the samples with higher molybdenum loadings, small crystallites of MoO_3 and the exchanged molybdenum species coexist on the zeolite. By careful deconvolution (see Figures S3, S4, and S5), it is clear that 78%, 58%, and 33% of molybdenum on 4Mo/HZSM-5, 6Mo/HZSM-5, and 10Mo/HZSM-5 are the exchanged molybdenum species, while the rest are present as molybdenum oxide crystallites.

It is well-known that during the MDA reaction, molybdenum species are reduced by methane to molybdenum carbide or oxycarbide.² Figure 2 illustrates the static ^{95}Mo NMR echo spectra obtained from a model compound, Mo_2C , and catalysts of 2Mo/HZSM-5 and 6Mo/HZSM-5 taken out of the MDA reaction at different time-on-stream. In general, the spectra of reacted catalysts all consist of at least two peaks; i.e., one broad peak that resembles bulk Mo_2C , and one much narrower peak similar to those of the fresh catalysts, but the center of the narrower peak is shifted downfield by about 30 ppm. It is most likely that Mo_2C was formed during reaction. For the case of the 2Mo/HZSM-5 catalyst after 15 min reaction, the narrower peak is of considerable intensity. However, for the 6Mo/HZSM-5 catalyst, regardless of the reaction time, the narrower peak has a much lower spectral intensity compared with that of the broader peak. This is probably because the exchanged Mo species in the reacted 6Mo/HZSM-5 catalyst have the opportunity of interacting with the conducting Mo_2C species and therefore exhibit a broadened spectral line due to the Knight-shift. Previous studies reveal that exchanged molybdenum species may form different types of carbides than the bulk Mo_2C ^{3d} (see note S1). Unfortunately, the broad nature of the spectra prevents us from giving an insightful analysis on the results. Nevertheless, the carburization process occurred for all the molybdenum species in the fresh catalysts.

Because all of the carburized molybdenum species originated from the species observed in Figure 1 (the so-called precursor of the carbide species), it is reasonable to correlate the amounts of the precursor species with catalytic performances to determine which species are the active sites for the MDA reaction. It is clear from Figure 3 that there is no linear relationship between the initial formation rate of the product aromatics and the quantities of total molybdenum species or MoO_3 crystallites (see note S2). Instead, a good correlation between the amount of the exchanged molybdenum species and aromatics formation rate is obtained. This demonstrates

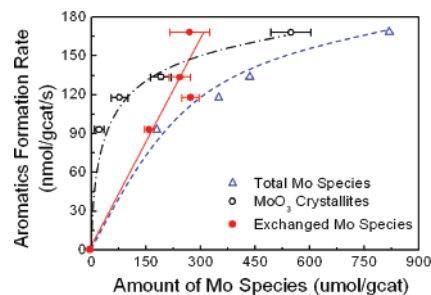


Figure 3. Correlating the aromatics formation rate with different molybdenum species.

that the carburized molybdenum species originating from the exchanged Mo species are the active centers for the MDA reaction.

In summary, direct observation of different types of molybdenum species on fresh and working Mo/zeolite catalysts by solid-state NMR is realized on an ultrahigh field NMR spectrometer. Coupling with the reaction data, it can be concluded that the exchanged Mo species are the active centers for the MDA reaction.

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Supporting Information Available: Details of the experimental procedures, the deconvolution results of ^{95}Mo NMR spectra of fresh catalysts, and notes S1 and S2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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