On the Dynamic Nature of Mo sites for Methane Dehydroaromatization

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Abstract: The mechanism of methane activation on Mo/HZSM-5 is poorly described, despite the great interest in methane dehydroaromatization (MDA) to replace oil refineries for producing aromatics. It is difficult to assess the exact nature of the active site due to fast coking. By pre-carburizing Mo/HZSM-5 with carbon monoxide, the active site for MDA can be isolated and studied without the formation of coke. This strategy helped us examine how methane is activated on the catalytic site by carrying out MDA using isotopically labelled methane ($^{13}CH_4$). We show that carbon originating from the pre-formed carbide is incorporated into the main products of the reaction, ethylene and benzene, demonstrating the dynamic nature of these active sites.

Keywords: Methane dehydroaromatization, Mo/HZSM-5, labelling experiments, molybdenum carbide

1. Introduction

For methane dehydroaromation (MDA), a great deal of research has focused on the most promising systems Mo/HZSM-5 and Mo/HMCM-22.[1, 2] The active phase for this catalyst, reduced Mo, was previously found to form in an initial period where no desired products are formed yet.[4-9] Several phases, MoC, Mo_2C, coke modified Mo_2C, Mo_2C on outside surface and reduced oxides in the pores of the zeolite, any kind of Mo^{6+} or partially reduced Mo^{6+} as $MoO_{(3-x)}$ are proposed as the active phase for this reaction, but no clarity on the exact nature has been achieved so far.[3] Observing the active site formation in the initial phase of MDA is difficult because of the simultaneous fast coking.

2. Experimental

Catalysts were based on a commercial HZSM-5 zeolite having Si/Al = 13 (HZ-13) and were prepared with 1, 2 and 5 wt.% loading (*x*) of Mo denoted as *x*MoHZ-*13* using $(NH_4)_6Mo_7O_{24}$ as a precursor.

3. Results and discussion

To understand the conditions necessary to prepare the active Mo site by CO carburization, CO consumption and simultaneous CO_2 production were monitored by mass spectrometry (MS) during Temperature Programmed Carburization (TPC) with $C^{18}O$. Figure 1 presents the typical profile of CO consumption and CO_2 production during CO carburization. It is evident from this figure that much less ^{18}O evolves as $CO^{18}O$ or $C^{18}O_2$ than what is consumed as $C^{18}O$, presenting proof that oxygen is part of the active Mo site. This supports previous claims that the active Mo site is in an oxycarbidic phase.[5, 6] Measuring *operando* X-ray absorption near edge structure (XANES), the reduction of a sample during catalyst activation under methane was compared with that of samples during carburization in CO. These experiments confirmed that after 1 h at 780 ^{0}C, CO reduces Mo to the same extent as achieved with CH_4, while reduction remains incomplete at 600 ^{0}C or 700 ^{0}C. The TPC and *operando* XANES experiments confirm that CO carburization can be used to produce an active Mo phase that is equivalent to the one forming during the activation period of the reaction with CH_4. This allows probing the interaction of CH_4 solely with the active Mo-carbide phase isolating this interaction from interactions with undefined (hydro-)carbonaceous species surrounding the active site, that would be present after carburization with CH_4. To understand how methane is activated on the reduced Mo species, we performed a series of pulsing experiments using labelled methane, $^{13}CH_4$.

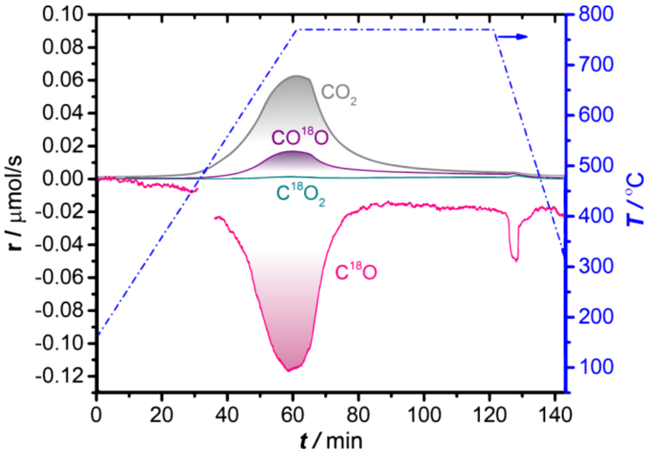

Figure 1. $C^{18}O$ consumption and simultaneous CO_2, $CO^{18}O$ and $C^{18}O_2$ production in TPC of 2MoHZ-13 with 30 ml/min, 2.5% $C^{18}O$ in He. Temperature was increased to 780 ^{0}C at a rate of 10 ^{0}C/min (right axis).

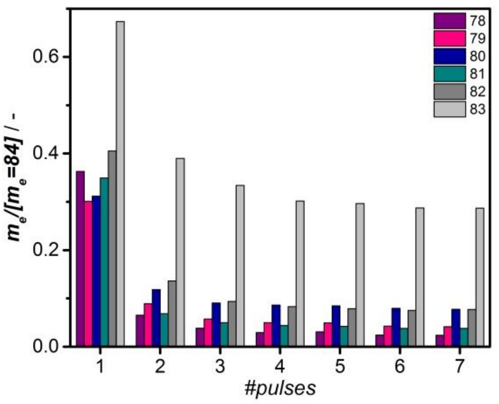

Figure 2. Evolution of area under each pulse for masses 78 to 83 typical for the fragmentation of benzene normalized by m_e = 84. under consecutive pulsing of 223 µmol $^{13}CH_4$ to 300 mg 2MoHZ-13 catalyst carburized at 780 °C with 30 ml/min 2.5% ^{12}CO in He.

Prior to this pulsing, the catalyst was carburized using ^{12}CO, forming ^{12}C based Mo-carbidic or -oxycarbidic species. This way, it was possible to track the incorporation of ^{12}C from the catalytic Mo site into the products. Firstly, masses 84 to 78 arising from fragmentation of labelled benzene, $^{13}C_6H_6$ as well as benzene where some ^{12}C is incorporated, were recorded on the MS. Figure 2 shows the abundance of the masses normalized by the one with highest abundance, $m/z = 84$. The ratio 83/84 is most informative in assessing the incorporation of ^{12}C into the observed benzene, because $m/z = 83$ is the most abundant mass for $^{12}C^{13}C_5H_6$ and should lead to a higher 83/84 ratio than for the control experiment where $m/z = 83$ only represents the $^{13}C_6H_5$ fragment. When using ^{12}C for carburization and ^{13}C for methane pulsing (Figure 2), the ratio of 83/84 reaches a value of 0.67 for the first pulse and decreases to 0.28 over the next 8 methane pulses. This value of 0.28 is the constant fragmentation ratio in the control experiment. The higher value of 83/84 during the initial pulses can clearly be attributed to the formation of $^{12}C^{13}C_5H_6$. Similarly development of mixed carbon isotopes was shown in ethylene, showing the incorporation of the carbide carbon in the product species.

4. Conclusions

We demonstrate that CO carburization is a powerful approach to isolate the formation of the active site in Mo/HZSM-5 for the non-oxidative methane conversion without producing undesired catalyst coking. This strategy allowed us to study, at the molecular level, the activation of methane on the Mo catalytic active site. We show that the catalytic Mo site actively takes part in the reaction rather than acting as an adsorption site to lower the activation barrier of CH_4. Rapid exchange reactions with the dynamic Mo-site results in the incorporation of carbidic carbon into the products ethylene and benzene. It provides a good starting point for finding the precise molecular structure of the reduced Mo formed as it demonstrates that the carbon at the metal site in this structure is easily replaced by another carbon from methane, pointing at a dynamic active site. Further, we provide proof that oxygen is present at the active site.

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