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Solid state ^{13}C NMR studies of methane dehydroaromatization reaction on Mo/HZSM-5 and W/HZSM-5 catalysts

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Methane dehydroaromatization on Mo/HZSM-5 and W/HZSM-5 catalysts was studied by solid state ^{13}C NMR spectroscopy, both variation of the state of transition metal component and products such as ethane, benzene, ethene adsorbed on or in zeolite were observed after high temperature (900–1000 K) reaction.

Catalytic conversion of methane to higher hydrocarbons remains an important challenge to chemists. Since 1993, considerable attention has been paid to the non-oxidative activation of methane to aromatics over Mo/HZSM-5 catalysts.[1–5] At present, it is generally accepted that the Brönsted acidity and channel structure of the zeolite as well as oxidation state of the transition metal component are crucial factors for the performance of this catalyst.[2] However, there are controversial views on both the reaction mechanism and the active phase of metals regarding this reaction.[3–7] Information directly from the surface of the catalysts in the process of the reaction is needed to understand the reaction, but the data on which to characterize the reaction is mostly from the off line gas phase detection. Solid state NMR has proved to be a powerful technique for characterizing structures of heterogeneous catalysts and elucidating reaction mechanisms. It can detect not only intermediates and products adsorbed in or on catalysts, but also the change of active sites in the process of catalytic reaction.[8–10] Recently, Ma *et al.*[11] observed the change of Brönsted acid sites and the formation of products, cokes in the process of methane dehydroaromatization over Mo/HZSM-5 by *in situ* ^{1}H MAS NMR. In this note, we studied methane dehydroaromatization reaction on Mo and W modified HZSM-5 catalysts by solid sate ^{13}C NMR spectroscopy for the first time.

Mo/HZSM-5 and W/HZSM-5 catalysts were prepared using procedures described in the literature.[11,12] HZSM-5 (Si/Al = 25) powder was impregnated with an aqueous solution containing a given amount of ammonia heptammolybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) or ammonium tungstate ($(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$) (in the latter case, the pH value of the solution was regulated to 2–3 by H_2SO_4), dried at room temperature for 12 h, at 373 K for 8 h and then calcined at 773 K for 5 h. Mo(or W)/HZSM-5 catalysts with different Mo(W) loadings were denoted as *x*Mo(W)/HZSM-5, where *x* is the weight percentage of the Mo(W) content in the sample. Due to their good catalytic performance, 6Mo/HZSM-5 and 4W/HZSM-5 catalysts were chosen for investigation. Molybdenum carbide was prepared as follows: 0.2 g MoO_3 was reduced and carburized with 20% CH_4/H_2 (30 ml min^{-1}) at 973 K for 8 h, then passivated with 1% O_2/He (20 ml min^{-1}) for 24 h. About 0.5 g Mo/HZSM-5 or W/HZSM-5 power was placed into a 5 ml quartz tube, and activated in vacuum (10^{-5} Torr) at 673 K for 5 h. 0.25 mmol methane (^{13}C, 99%, Cambridge Isotope Inc.) was introduced at room temperature under vacuum and frozen on the catalyst with liquid N_2 and then the quartz tube was sealed. The sealed ampoules were heated at different temperatures for a specific period and then reaction was quenched by liquid N_2. Prior to NMR measurement, the sealed ampoules were opened and the samples were transferred into a 7.5 mm ZrO_2 rotor (sealed by Kel-F cap) under a dry nitrogen atmosphere in a glove box. All the NMR experiments were carried out at 9.4 T on a Varian Infinityplus-400 spectrometer, equipped with a Chemagnetic triple-resonance 7.5 mm probe, with resonance frequencies of 400.12 and 100.4 MHz for ^{1}H and ^{13}C, respectively. Single pulse ^{13}C MAS (with ^{1}H decoupling, 1pda) and $^{1}H/^{13}C$ CP/MAS experiments were performed with 4 and 2 s relaxation delays, respectively. The contact time of CP experiments was set to 1 ms. A spatially selective composite pulse was combined with conventional 1pda and CP pulse sequences in order to effectively suppress weak signals (background) from the spinning module.[13]

Fig. 1 shows the ^{13}C spectra of methane reaction on 6Mo/HZSM-5 at different temperatures. After adsorption of methane on 6Mo/HZSM-5 at room temperature, only the resonance of adsorbed methane was observed at −8 ppm (Fig. 1(a), the weak resonance at 112 ppm is due to the background of the probe). After reaction at 873 K for 60 min (Fig. 1(b)), the intensity of signal of methane decreases dramatically and a strong signal at 126 ppm appears, which can be assigned to CO_2.[14] However, only the signal of methane is detected in the corresponding ^{13}C CP/MAS NMR spectrum (not shown here). After reaction at 973 K for 30 min, new peaks at 184, 274 ppm appear in the ^{13}C MAS spectrum (Fig. 1(c)), together with an increase of the intensity of peak at around 126 ppm. These new peaks are not observed in the corresponding CP/MAS spectrum (Fig. 1(d)). We also repeated the CP experiments with a longer contact time (4 ms) and did not observe the signals at 126, 184 and 274 ppm, probably indicating that they correspond to carbon species that are not in close proximity to protons. According to its chemical

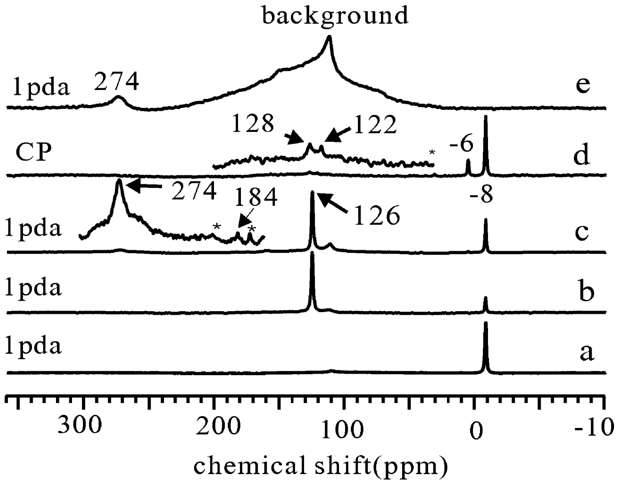

Fig. 1 ^{13}C MAS NMR spectra of methane (^{13}C, 99%) reaction on 6Mo/HZSM-5 at (a) room temperature, 1 pulse with ^{1}H decoupling (1pda); (b) 873 K for 1 h, 1pda; (c) 973 K for 30 min, 1pda; (d) 973 K for 30 min, CP. For comparison, ^{13}C MAS NMR spectrum of molybdenum carbide powder is shown in (e). The spectra were recorded at room temperature. Asterisks denote spinning sidebands. The signal at 112 ppm is due to background of spinning module.

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shift, the 184 ppm peak can be attributed to formation of CO,[8,14–15] while the 274 ppm peak is likely due to carbidic carbon of molybdenum carbide. In order to confirm this assignment, we prepared a molybdenum carbide sample and recorded its ^{13}C MAS spectrum. As shown in Fig. 1(e), molybdenum carbide actually gives rise to a resonance at 274 ppm. It was reported that an induction period exists for methane dehydroaromatization reaction and molybdenum oxide will be transformed into molybdenum carbide during the reaction, leading to the formation of CO_2, CO and water.[16] Our results strongly support the previous observation. Although only a weak signal at 6 ppm (which was attributed to ethane[14]) is observed in Fig. 1(c), it is selectively enhanced in CP/MAS NMR spectrum (Fig. 1(d)). Meanwhile, the two signals at 122 and 128 ppm in the corresponding CP/MAS spectrum can be assigned to adsorbed ethene and benzene on the catalyst surface,[14] respectively.

It should be noted that the resonance of molybdenum carbide (Fig. 1(d)) is actually an overlap of a broad peak and a narrow one, suggesting that molybdenum carbide is present in different chemical environments. Previous investigation suggested that Mo species are highly dispersed in/on the zeolite in the process of impregnation and calcination.[3] We tentatively assign the narrow signal to molybdenum carbide on the external surface of the zeolite and the broad one to molybdenum carbide residing in the channels, intersections of channels and crystalline defects of ZSM-5. The difference of the chemical environments of the molybdenum carbide leads to a broad distribution of its chemical shift. Our ^{13}C solid state NMR experimental results agree well with the previous ^{1}H NMR results, but the formation of molybdenum carbide and some products such as ethane and ethylene which were not detected in ^{1}H NMR are visible in the present case, showing the efficiency of the ^{13}C NMR in elucidation of the catalytic reaction.

The similar properties of Mo and W suggests that W/HZSM-5 should present similar features to Mo/HZSM-5. However, as demonstrated by ^{13}C NMR experiments, W/HZSM-5 catalyst shows some different features for the methane dehydroaromatization. After heating to 873 and 973 K (Fig. 2(b) and 2(c)), the CO_2 formed on 4W/HZSM-5 is much less than that formed on 6Mo/HZSM-5 under the same reaction conditions. The Mo/W mole ratio is about 3:1 for the same mass of 6Mo/HZSM-5 and 4W/HZSM-5 catalysts, but the ratio of CO_2 formed during the reaction is *ca*. 5.5:1 (by comparing the amount of CO_2 in Fig 1(b) to that of Fig 2(b), or Fig 1(c) to that of Fig 2(c)). This means that for the same mole content of Mo and W in the catalysts, only *ca*. 50% W oxide is reduced by methane in the induction period if 100% Mo oxide is reduced, indicating that W oxide is probably more difficult to be reduced by methane. Recently, Ding *et al.*[17] observed the WC_x cluster by XANES on a 6W/HZSM-5 catalyst (prepared by solid exchange method) after 1 h methane aromatization reaction and concluded that the WC_x species are responsible for initial activation of methane. Although the reaction products such as ethane, benzene and CO were observed in our ^{13}C NMR spectra (Fig. 2 (d) and Fig. 2(c)), no carbide tungsten was detected, even after reaction at 1023 K for 1 h (Fig. 2(e)). There are three possibilities that could lead to the difference. One is the relatively lower concentration of WC_x formed on the 4W/HZSM-5 catalyst, which makes the species beyond detection. The other is the different sample preparation method with respect to that of Ding *et al*. The third is that the W oxide is probably reduced by methane in the induction period to other oxide states such as WO_x.

$$WO_3 + CH_4 \rightarrow WO_x + CO + CO_2 + H_2O$$

In this case, it is likely the WO_x rather than WC_x that acts as the active phase for methane activation. Lunsford *et al.*[18] did not detect the formation of WC_x species during the methane dehydroaromatization by XPS technique either.

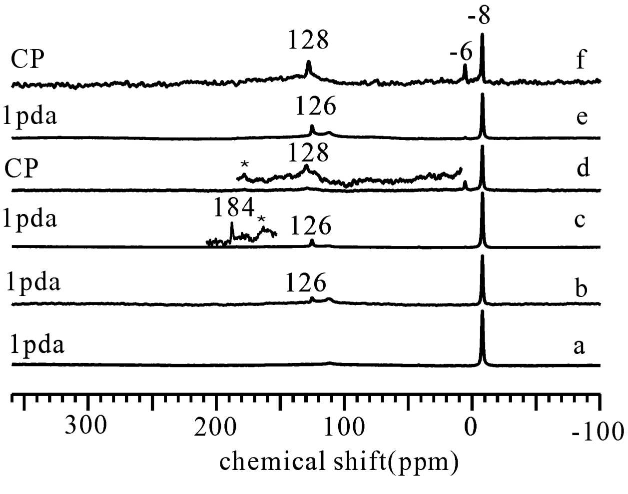

Fig. 2 ^{13}C MAS NMR spectra of methane (^{13}C, 99%) reaction on 4W/HZSM-5 at (a) room temperature, 1pda; (b) 873 K for 1 h, 1pda; (c) 973 K for 30 min, 1pda; (d) 973 K for 30 min, CP; (e) 1023 K for 1 h, 1pda; (f) 1073 K for 1 h, CP. The spectra were measured at room temperature. Asterisks denote spinning sidebands. The signal at 112 ppm is due to background of spinning module.

In summary, methane dehydroaromatization on Mo/HZSM-5 and W/HZSM-5 was studied by solid state ^{13}C NMR spectroscopy, both variation of the state of transition metal component and products such as ethane, benzene, ethylene adsorbed on or in zeolite were observed after high temperature (900–1000 K) reaction. It is confirmed that two different kinds of molybdenum carbide formed during the reaction, which are assigned to molybdenum carbide dispersed on the external surface and internal channel of zeolite, respectively. The detailed information from the surface of the catalysts reveals what happen in the initial induction period and will help us to understand the mechanism of this reaction. Further investigation is still in progress.

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