SURFACE ANALYSIS OF MO/HZSM5 CATALYST PREPARED BY MICROWAVE HEATING FOR NON-OXIDATIVE AROMATIZATION OF METHANE

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Introduction

The direct conversion of methane into hydrogen and other high-value-added products such as aromatics has recently attracted considerable attention. It makes the natural gas resource become one attractive feed which produce the aromatic hydrocarbon products following petroleum, and open up the new route to the utilization of natural gas resources.

There has been a general agreement that methane aromatization catalyzed by Mo/HZSM-5 has been recognized as a promising route for producing aromatics in an oxygen-free atmosphere [1-2]. Several factors such as the acid site density, the zeolite channel structure, and the oxidation state and location of the molybdenum species have been recognized to affect the performance of methane conversion into aromatics[3-4]. Despite prolific research activity worldwide, progress in this field has been hampered by serious catalyst deactivation, which is responsible for the decrease in conversion into useful products. As the performance of the catalyst often depends on surface status, and the surface status of catalyst is related with the preparation method, it is therefore necessary to seek better preparation method and analyze surface species for improving the catalyst performance.

Nowadays, the impregnation method is the major method for its easier operation and economical cost. The novel method i.e. microwave heating is recently applied in the oxidative coupling of methane. Seen from the results of reaction, the performance of catalysts prepared by microwave heating is better than that of catalysts prepared by impregnation, and this method is also very simple. Here a series of catalysts are prepared by microwave heating, the oxidation state and location of the Mo species were analyzed by XRD, and the surface distribution of catalysts and form of carbon deposit of catalysts after reaction were investigated by TEM.

Experimental

Catalysts preparation The zeolite [HZSM-5, (Si/Al=25), from Nankai chemical reagent factory of China] and the required amount of ammonium heptamolybdate [$(NH_4)_6Mo_7O_{24}.4H_2O$, from Jinduicheng molybdenum chemical division of china] were mechanically mixed, subsequently, the mixtures were calcined under proper power in the microwave oven for some time, and then the solid samples were pressed, crushed, and sieved to separate catalyst grain in the size range 20-35 mesh for subsequent use in aromatization reactions. In addition, the same Mo loading catalyst is prepared by impregnation so that there is the contrast between two methods on the characterization of catalyst.

Reaction testing Catalysts reaction testing has carried out at atmospheric pressure by a fixed-bed continuous flow system with a quartz reactor of 8-mm-i.d., in which 0.5 g of catalyst was loaded. It was connected to a gas feeding unit and analytical equipment. The reaction temperature 973K was controlled by a sheathed thermocouple embedded in a 35-mm-high catalyst layer. CH_4 was fed to the reactor at mass-flow controlled rates sweeping the methane hourly space velocity range of 3600mL (STP) $\cdot h^{-1} \cdot g^{-1}$. The gaseous reaction products were analyzed by means of a HP gas chromatograph equipped with a flame ionization detector (FID) connected to a PLOT-Q capillary column (30 m long and 50μm i.d.) supplied by J&W Scientific Cop.

Catalysts characterization The surface species analysis of catalysts was carried out with the RIGAKUD/MAX-2400 diffract meter by Rigaku Corporation of Japan using Cu Kα radiation at 36kV and 80mA. The spectrums were recorded over a 2θ range of 5º--60º at a scanning rate of 5º min^{-1}. The surface states of catalysts before and after reaction were carried out using JEM-200CX Transmission Electron Microscope supplied by Electric Corporation of Japan. The samples were dispersed in ethanol reagent, and then one of them was selected and suspended on the copper web for analysis under different multiple of enlargement.

Results and discussion

XRD analysis Figure 1 showed the XRD spectrum of 6% Mo based catalysts prepared by different methods, in which spectrum 1 is the XRD spectrum of catalyst prepared microwave heating, spectrum 2 is catalyst prepared by impregnation, and spectrum 3 is the used catalysts prepared by microwave heating. Seen from figure 1, all of spectrums have a majority of same peaks with the XRD spectrum of HZSM5 from corresponding literature[5], but the loading of Mo species makes the characteristic diffraction peaks lower. It reveals that the Mo species on the HZSM5 are dispersive relatively. There are three characteristic diffraction peaks of MoO_3 species when 2θ is about 30º in all spectrums; the MoO_3 species signal in spectrum1 is higher than that in spectrum 2. It's implied that most of MoO_3 species spread the outer surface of the catalyst prepared by microwave method. The main reason of this phenomenon is the difference of calcination mode of catalysts. The microwave heating have the characters of high speed and from inside to outside compared with conventional heating, as the result of it, the shift of Mo species from outer surface to inner channel of zeloite stopped and the blockage of zeolite channel could be avoided. It leaded to the higher selectivity to benzene of catalysts. Compared with specturm1, 2 and 3, all of characteristic diffraction peaks sharply decreased in spectrum 3, the new characteristic diffraction peak was found when 2θ is about 39º. That's because the carbon accumulated at a higher rate on the surface of catalyst, blocked active sites and thus caused gradual deactivation. The new characteristic diffraction peaks occurred was thought as Mo_2C species according to literature [6]. It is consist with the statement that Mo occurred as molybdenum carbide (say Mo_2C) under reaction conditions. The Mo_2C is real active species during reaction.

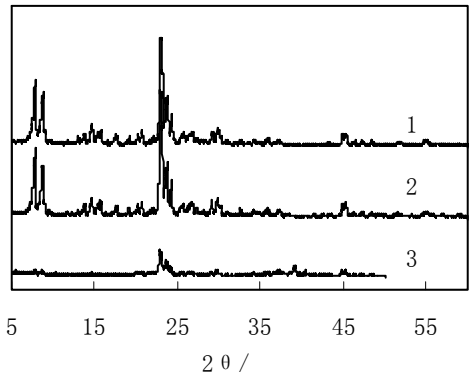
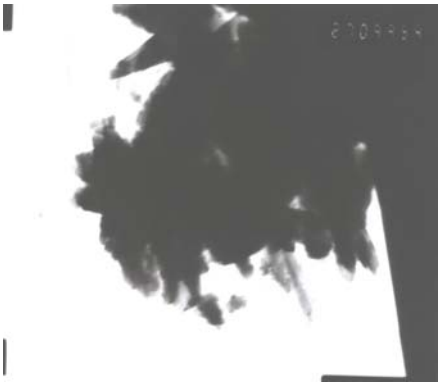


Figure 1. XRD spectrum of a series of 6% Mo/HZSM5 catalysts

TEM analysis Methane aromatization is an endothermic equilibrium-controlled reaction, and the high temperature is required to yield meaningful conversions into aromatics during the reaction. However, such severe conditions are favorable for carbon deposition.

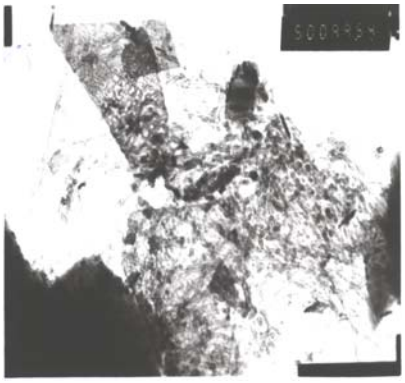


2a. 27×1000 before reaction

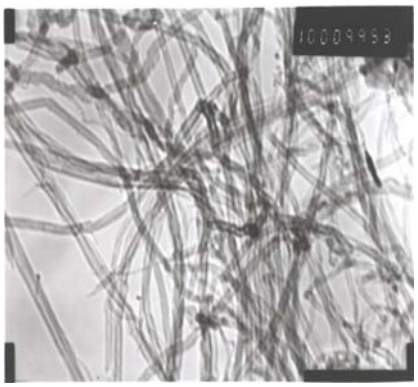
2b. 180×1000 before reaction

They occurred as the form of carbon nanotube during the reaction. Figure 2 showed the TEM pictures of 6%Mo/HZSM-5 catalyst before and after reaction. Figure 2a and 2b showed the surface state before reaction under different multiple. Seen from figure 2a, the massive material in the right is the HZSM-5 zeolite, and the Mo species are in the middle. The active Mo species was closely attached to carrier. Figure 2b was obtained under 180×1000 multiple. It showed the surface distribution of catalyst clearly. The size of Mo species is 20~30 nm, which is much larger than that of ZSM-5 zeolite channel (0.54nm×0.56nm), so the most of Mo species should be spread the outer surface of carrier, the active species were highly dispersed on zeolite. It is consistent with the results of XRD analysis. No fibriform material can be seen on surface of catalyst in figure2a and 2b.

Figure 2c and 2d are the TEM pictures of catalyst under different multiple. They represent the surface carbon deposit of catalysts after reaction. Seen from figure2c, the fibriform materials are winding on the surface of catalyst, which indicates that the coke occurred. In the figure 2c, the fibriform materials are the carbon deposit and the massive material is carrier. Figure 2d was pictured under 100×1000 multiple. A brunch of tubular material can be seen clearly. They are the carbon nanotubes due to carbon accumulation. One end of each carbon nanotube was attached to catalyst, the other end extended to outside. They are slim and have same size range of 10-20 nm. The similar phenomenon was reported in Ni catalysts[7]. As the Brønsted acid site is the major position of accumulating carbon deposits at high temperature, in addition to the existence of Mo species on the surface of zeolite, the carbon nanotube generate under interaction of Mo species and the Brønsted acid site, then stretch out towards outside.



2c. 50×1000 after reaction



2d. 100×1000 after reaction

Figure 2. TEM picture of 6% Mo/HZSM5 catalysts before and after reaction

Conclusion

The analysis of XRD showed that the Mo species highly dispersed on outer surface of carrier for catalyst prepared by microwave heating method. Mo_2C is the real active species during the reaction, and its characteristic diffraction peaks can be found on surface of catalyst after reaction. Analysis of TEM further proved the high dispersion of Mo species. The size of Mo species is 20-30nm. The form of carbon deposit in methane aromatization is the hollowed carbon nanotube. The size of them is 10-20 nm. They grew up with the carbon accumulation.

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