

Coke species and coking mechanism of SAPO-34 in MTO process

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The coking behavior of SAPO-34 in MTO process was investigated. The primary dynamics of coking, the characteristics of coke species and effect of coke deposition on catalyst performance were studied by means of reaction evaluation, TG-DTA, temperature-programmed cracking test, IR and GC-MS. It was found that the coke species formed at different reaction temperatures were different. The coking mechanics at different reaction temperature was supposed to be different.

1. INTRODUCTION

As a MTO catalyst, SAPO-34 has been of great interest for its high selectivity for ethene in MTO reaction, which is ascribed to its pore size restriction and suitable acidity^[1-5]. However, its small pore size, as well as the supercage-window structure, causes rapid coking and deactivation in the reaction. Several literatures have reported the coking behavior of SAPO-34^[6-9] in MTO reaction. In the present study, we investigated the coking behaviors in MTO reactions and tried to find out the relationship between the reaction temperature and coke species or coking mechanism.

2. EXPERIMENTAL

H-SAPO-34 with an atom ratio of 0.3Si:0.8P:Al was used in all tests. SAPO-34 was synthesized by hydrothermal method, using triethylamine as template, as described in literature [10]. The as-synthesized SAPO-34 was calcined at 550°C for 3 hours to be converted to H-type. The MTO reactions over H-SAPO-34 were carried out in a fixed bed reactor at different reaction temperatures. The catalytic performance was evaluated using an online Shimadzu GC-9AM chromatogram analyzer equipped with a FID detector and a tree-meter Porapak-Q column. Methanol was evaporated, diluted with nitrogen and fed into the reactor at partial pressure of 0.1 atm and WHSV of 0.06 hr⁻¹. The reaction was carried out at 350°C and 550°C respectively. In order to obtain samples with evenly distributed coke, the catalyst bed was made very thin.

The coking dynamics tests and the determination of coke amount after reaction was carried out on Perkin-Elmer TGS-2 and DTA 1700 analyzers. Methanol diluted in helium of 20cc/minute, at partial pressure of 0.025atm, was introduced for the coking dynamics tests. IR spectra of the coked samples were measured on a Perkin-Elmer 983G IR spectrophotometer. Temperature programmed cracking tests of coked samples were designed and carried out on a

homemade apparatus. The samples were heated in helium at the temperature-rising rate of 15°C/minute. The out-let gas was detected with a TCD. Some coked samples were smashed and extracted with CCl₄. The extracted substances were analyzed using an Agilent 4890-5973 GC-MS. Analyzer.

3. RESULTS AND DISCUSSION

Coking dynamics curves of SAPO-34 at different reaction temperature and the effects of temperature on coking dynamics were shown in Figure 1 and Table 1, respectively. It is clear that the final amount of coke deposit decreases with increasing temperature at first, and then gradually approaches a stable value above 450°C. In the temperature range of 400~550°C, the initial rate of coke formation increases with increasing temperature. It is interesting that at the reaction temperature of 350°C maximum values are obtained for both the coke deposit and the initial rate of coking (3.8×10^{-3} g/g.min.). It is also interesting that the samples coked at different reaction temperature present different color. On the TG-DTA diagrams of coked samples in temperature programmed oxidation (Figure 2), only one exothermic peak at temperature of 560°C appears when reaction temperature is 550°C, while appear two exothermic peaks at temperature of 420°C and 520°C, respectively, when reaction temperature is 350°C. It is obvious that coke species with different burning rates formed at different reaction temperatures. IR spectra of coked SAPO-34 samples are shown in Figure 3. The coke formed at 350°C presents two absorbent bands. The band from 1650 cm⁻¹ to 1450cm⁻¹ is ascribed to aromatics^[11,12], while the band from 1450cm⁻¹ to 1350cm⁻¹ is ascribed to aliphatic species^[13,14]. The coke formed at 550°C presents mainly the absorbent band for aromatics. We can conclude that different coke species formed at different reaction temperatures. The coke formed at 350°C contains species of higher H-saturation, i.e., and aliphatic hydrocarbons. J. M. Campelo and co-workers reported similar results^[7]. They found some heavier oligomers formed inside the supercage and could not leave the cage, leading to pore blockage.

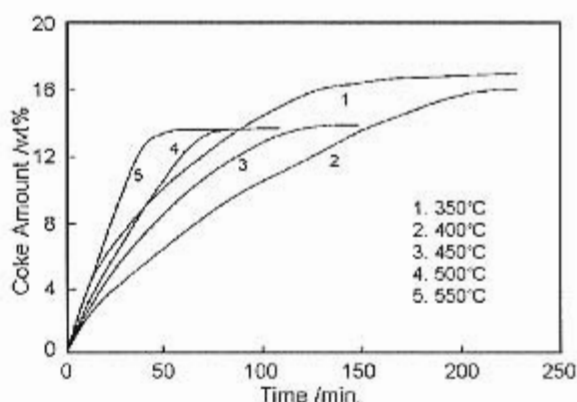


Fig.1 Coking dynamic Curves of SAPO-34 at different reaction temperature

Table 1
Effects of temperature on coking dynamics

Reaction temperature (°C)	350	400	450	500	550
Final amount of coke deposit (g/g)	16.82	15.59	13.75	13.65	13.61
Initial coking rate (g/g.min.)	3.8×10^{-3}	1.9×10^{-3}	2.3×10^{-3}	2.9×10^{-3}	3.7×10^{-3}
Color of coked samples	Brown	Green	Dark green	Black	Black

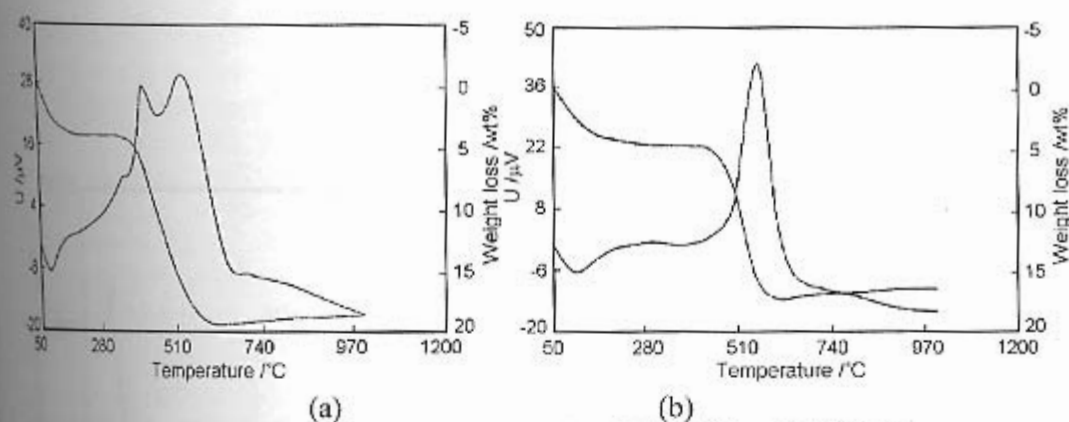


Fig.2 TG-DTA Curves of samples coked at 350°C (a) and 550°C (b)

The temperature programmed cracking (TPC) test of coked samples revealed that some coke species could be cracked to gases by heating in inert gases or in vacuum. Figure 4 describes the TPC curves of samples with different coke contents. The coke formed at 350°C gives TPC peaks at about 510°C, while coke formed at 550°C gives peaks at about 570°C. From the plots of TPC curve areas against coke content, it could be found that these crackable species consist mainly in lower-temperature coke and/or coke at low contents (Figure 5). IR study shows that these crackable species are aliphatic (Figure 6). The absorbent band of 1450-1350 cm^{-1} appeared when the samples were heated in vacuum. It was found by GC analysis that the out-let gas in TPC consisted of C1-C3 alkanes and alkenes. This suggests that these crackable coke species be oligomers.



Fig.3 IR spectra of samples of SAPO-34: (a) fresh; (b) coked at 350°C, 3.8wt%; (c) coked at 450°C, 4.29wt%; (d) coked at 550°C, 2.89wt%.

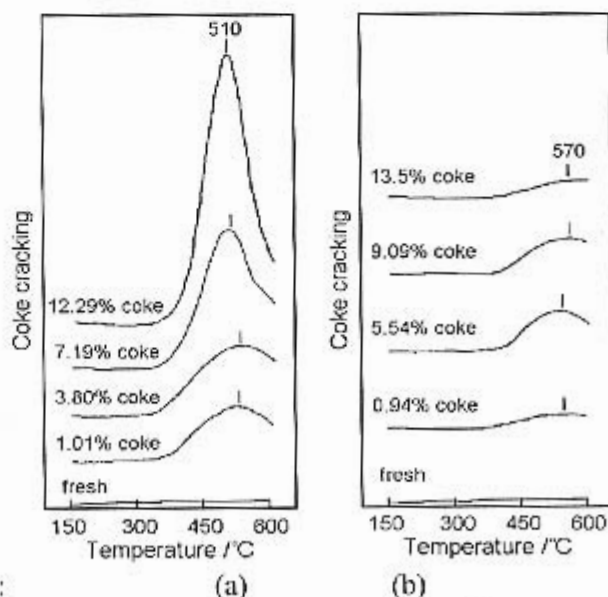


Fig.4 Temperature programmed cracking curves of samples coked at 350°C (a) and 550°C (b)

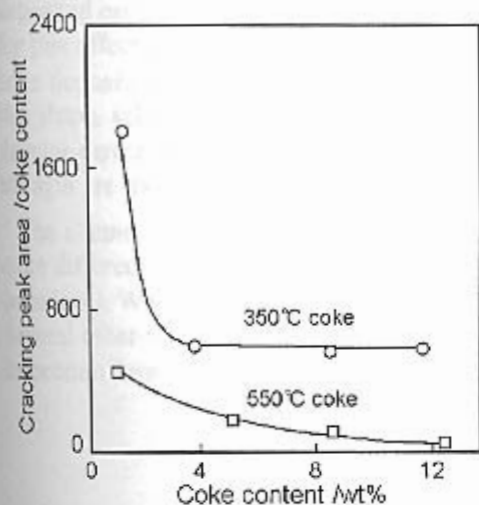


Fig. 5 Cracking peak areas / coke content versus coke content

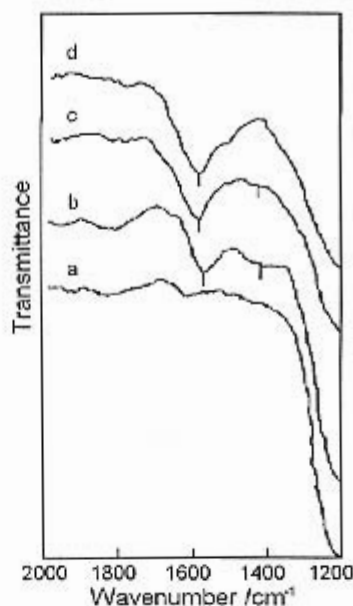


Fig. 6 IR spectra of samples in TPC: (a) fresh; (b) coked at 350°C, 3.8wt%; (c) sample b degassed at 400°C, (d) sample c degassed at 450°C

Although the initial coking rate was rapid, it had no significant effect on methanol conversions at reaction temperatures of both 350°C and 550°C, owing to the low WHSV we used. Also, it can be concluded from the rather high coke amount that a large amount of

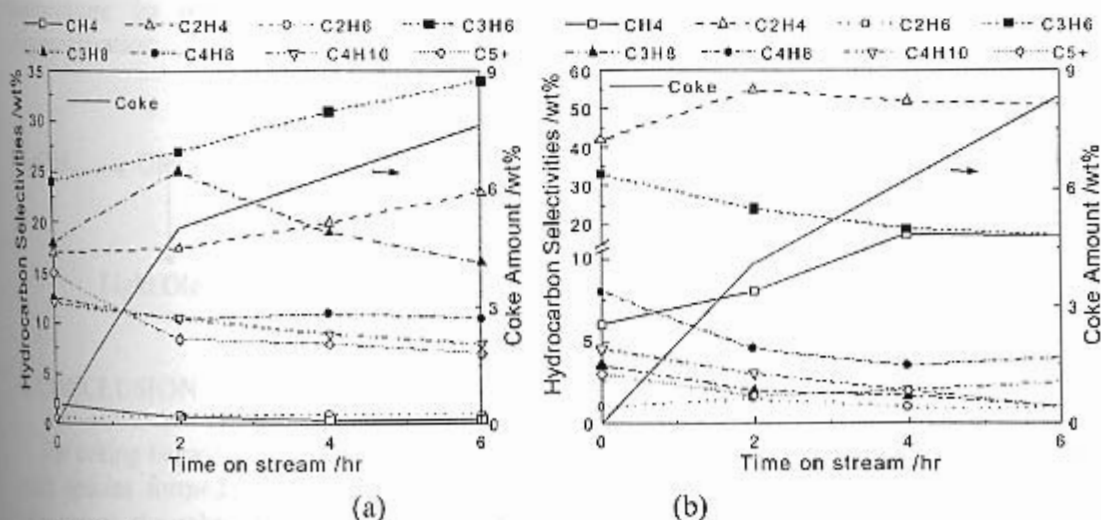
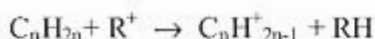


Fig. 7 Hydrocarbon selectivity and coke formation of MTO reaction versus time on line: reactions were carried out at 350°C (a) and 550°C (b), respectively

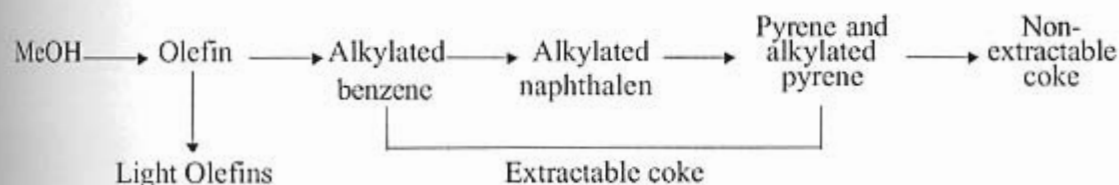
methanol fed was converted to coke. Thus the product distribution of the out-let gas should be closely related to the coking process. At reaction temperature of 350°C, initial coke had no notable effect on selectivity for ethene, which increases slowly with increasing time on stream (Figure 7a). At 550°C, ethene selectivity raised remarkably after even very little coke deposited on catalyst, and then leveled off in the ensuing aging course (Figure 7b). The reason for this effect may be contributed by the fact that at higher reaction temperature the initial coke deposits on the external surface and partly blocks the pore mouths therefore enhances the shape selectivity for ethene. Another reason may be that the initial coke forms and develops over the strong acid sites and covers them, and the remained acid sites of medium strength are more favorable for the ethene selectivity.

The alkane distributions in the hydrocarbon products at different reaction temperatures are quite different. At 350°C, the selectivity for C₂-C₄ alkanes is high and decreases with raising coke level. We suspect that the formation of alkane may be directly related to coking process. Several other researchers reported^[15-18] that alkanes can be generated from the formation of carbenium ions:



Also, the alkyl carbenium ions can further react with olefins to produce alkanes and adsorbed species of less H-saturated alkylene carbenium ions, via hydride transfer over L acid sites. Further hydride transfer and cyclization of alkylene carbenium ions lead to the formation of aromatics. The aromatics and/or together with oligomers finally form coke of different H-saturation.

The above-mentioned scheme may explain the coking behaviors at lower temperature. However, at higher temperature (i.e. 550°C), methane becomes the dominant component in the alkane products. It seems that different reaction temperatures make the coking mechanisms different. The components of the substance extracted from the catalyst samples coked at 550°C, analyzed by using GC-MS, are a variety of aromatics- from alkylated benzenes to alkylated pyrenes. No oligomers were detected. We suggest that conking at higher temperature go on via aromatization, as the following scheme shows, but not via oligomerization:



4. CONCLUSION

The coking behavior of SAPO-34 in MTO process was investigated. It was found that the coke species formed at different reaction temperatures were different. At lower reaction temperature, the coke consists of both aromatics and oligomers. When reaction temperature is

high, the coke is mainly aromatic. It is suggested that the coking mechanism at different reaction temperatures go on via different route, i.e. via oligomerization at lower temperature while via aromatization at higher temperature.

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