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The effect of dealumination on the apparent and actual rates of aromatization of methane over MFI-supported molybdenum catalysts

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Abstract

Molybdenum carbide associated with a surface dealuminated H-MFI appeared to be more active and more stable than when associated to the parent H-MFI, contrary to the expectation, in the conversion of a 1:1 mixture of methane and argon at atmospheric presssure and low flow rate (HPLF experiment). By contrast, under a low methane partial pressure and a high flow rate (LPHF experiment), the expected order of activity was found; the carbide associated with the parent zeolite showed a significantly higher activity. The discrepancy shown by the results of the two sets of experiments was interpreted in terms of a more rapid deactivation of the most active catalyst under a high methane load, resulting in a lower apparent activity. The higher stability of the carbide associated with the surface dealuminated zeolite resulted from the elimination of the surface sites which produce bulky aromatics with low vapor pressure leading to a rapid clogging of the pore mouths of the zeolite, in line with the general background on zeolite catalysis.

Keywords: Methane; Dehydrocyclization; Surface dealumination; Mo-ZSM-5; Catalyst deactivation

1. Introduction

Conversion of methane into useful chemicals has been and still is a subject of worldwide renewed efforts. Several routes have been explored over the previous two decades. In addition to methane conversion into syngas which is of real industrial significance, more ambitious routes such as direct conversion into oxygenates [1–4], methanation of olefins [5], oxidative coupling of methane [6–9], and conversion of methane into benzene and hydrogen were explored [10–27].

The latest developments were concerned with the latter reaction carried out in the presence of various transition-metal oxide-loaded inorganic carriers. Mainly molybdenum- and rhenium-based active components deposited over HZSM-5 were thoroughly investigated [22–27].

In the case of molybdenum-based catalysts, the activation procedure was scrutinized and it was generally agreed that whatever the nature of the precursor, molybdenum was converted, in the presence of methane, under the reaction conditions, into molybdenum carbide [12,13,24]. Quite recently, Derouane and colleagues have shown that it was possible to synthesize bulk or supported metastable fcc molybdenum carbide with a formula MoC_{1-x}. H-MFI-supported fcc carbide exhibited higher activity and stability, and selectivity to benzene in the dehydrocyclization of methane than the hexagonal β Mo_2C. Unfortunately, its higher selectivity to benzene, very likely to be the major reason for its better stability, was not investigated further [28–30].

As far as the reaction was concerned it was generally accepted that the reaction proceeded via the formation of C_2H_2 (or C_2H_4) over the molybdenum carbide species and further cyclization and aromatization would occur over the acid sites. The successive set of reactions would produce, via alkylation of benzene, various aromatics among which naph-

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thalene was the most frequently mentioned, although molecules such as toluene, xylenes. and divinylbenzene were also reported.

Interestingly, the most abundantly produced molecule, i.e., H_2, was not always analyzed quantitatively. Also given the rather high temperature domain, due to thermodynamic limitations, various carbon species were formed which escaped analysis and resulted in a gradual deactivation of the catalyst.

A number of studies were aimed at probing the nature of these carbon species and at identifying their nature, location, and mode of formation [31,32].

Recently, as Iglesia and co-workers reported [21], silanation of the HZSM-5 carrier was carried out in an effort to decrease the density of external surface acid sites, on the one hand, and the number of molybdenum precursors retained at these external sites as a result of ion exchange thought to occur upon physically mixing the HZSM-5 with MoO_3 and subsequent activation, on the other hand.

They showed conclusively that the silanation did not affect the nature of the MoOx precursor of the active species assumed to be molybdenum carbide. However, they report that significant improvements were observed not only with respect to selectivity and stability as expected, but also surprisingly with regard to the activity upon silanation of the HZSM-5 carrier in the pyrolysis of methane [21].

In an effort to understand the reason(s) of these improvements and the specific effect of the external sites we investigated the catalytic performance of a similar molybdenum-based HZSM-5 system where external surface sites were eliminated via selective dealumination by oxalic acid.

2. Experimental

The starting HZSM-5 was synthesized from a batch with the composition 0.1 SiO_2:0.04 TPAOH:0.004 $Al(NO_3)_3$:$5H_2O$ at the synthesis temperature of 175 °C over a period of 24 h. Tetraethylorthosilicate (98%, Aldrich) as the silica source, aluminum nitrate (Aldrich) as the aluminum source, 1 M tetrapropylammonium hydroxide solution (Aldrich) as the organic template, and deionized water were used in the synthesis. After synthesis, the as-synthesized zeolite was thoroughly washed with deionized water, filtered, and dried at 110 °C. Then it was calcined first under N_2 and then O_2 flow at 500 °C to remove the organic template. XRD showed the product to be a highly crystalline MFI zeolite. ^{29}Si NMR gave a Si/Al ratio of 21, in agreement with chemical analyses. No nonframework aluminum was detected. By contrast, the Si/Al ratio as measured by XPS was originally 11.6.

The dealumination was carried out by stirring 4 g of zeolite in 300 ml of 1 M aqueous oxalic acid at 70 °C for 2 h. The zeolite was then separated by centrifugation and thoroughly washed with deionized water. The final Si/Al ratio as determined by XPS was 21.4, while the overall ratio, as determined via chemical analysis and ^{29}Si NMR, was 25. Again no nonframework aluminum was detected. Ammonia TPD confirmed the modest but significant acidity decrease, since the parent zeolite retained 780 µmol per gram, while the dealuminated sample retained only 640 µmol per gram.

Both the original and dealuminated zeolites were loaded with molybdenum by the incipient wetness method using appropriate amounts of the zeolite and ammonium paramolybdate so as to achieve a nominal molybdenum content of 4% by weight. The molybdenum content was found to be 3.9% by weight for both zeolites, close to the nominal value, by chemical analyses. The impregnated zeolite was finally dried at 110 °C. A 300-mg sample of the dry powder was placed in a U-shaped quartz reactor with 14-mm inner diameter and was heated in flowing O_2 at 650 °C.

In one type of catalytic experiments, labeled as low-pressure (LP) experiment, the catalyst was subjected overnight to a 730:30 H_2:CH_4 mixture (total atmospheric pressure) at 700 °C, to achieve carburization of the supported/exchanged Mo species and prevent the occurrence of metallic molybdenum and/or the deposit of carbon [27]. Following this treatment, XRD lines at about 34.5 and 39.5 2θ angles, apart from the diffraction lines of the MFI structure, were seen, indicating that the procedure recommended by Boudart et al. was indeed appropriate to obtain the Mo_2C carbide. The carburized catalyst was then reacted with a 24:736 CH_4:Ar mixture at a flow rate of 13 L/h, at the same temperature, and the products were analyzed.

In a second set of experiments, labeled as high-pressure (HP) experiments, the molybdenum-loaded zeolite was simply not precarburized but submitted directly after the O_2 treatment and argon purge to an atmospheric mixture of 380:380 CH_4:Ar at 700 °C under a total flow rate of 0.75 L/h. Carburization was, thus, achieved concomittantly with the methane aromatization.

Products were analyzed in line using three gas chromatographs, two of them equipped with F.I. Detectors and columns packed with unibeads 35 to analyze aliphatics and with bentone to analyze aromatics. The third chromatograph equipped with a thermal conductivity cell detector and a column packed with carbosieve S was devoted to the analysis of CO, CO_2, and mainly H_2. Coke production was calculated on the basis of the evolved hydrogen in excess to that stoichiometrically produced upon the formation of all detected products (for example, $2CH_4 \rightarrow C_2H_4 + 2H_2$ or $7CH_4 \rightarrow C_7H_8 + 10H_2$) and assuming that coking was occuring according to the simple decomposition of methane into carbon and hydrogen.

3. Results and discussion

In the LP experiment it was noted that the conversion of methane did not experience an induction period as was the case in the HP experiment. This is ascribed to the fact that the catalyst of the LP experiment was carburized prior to the catalytic reaction. The active centers, which are accepted to

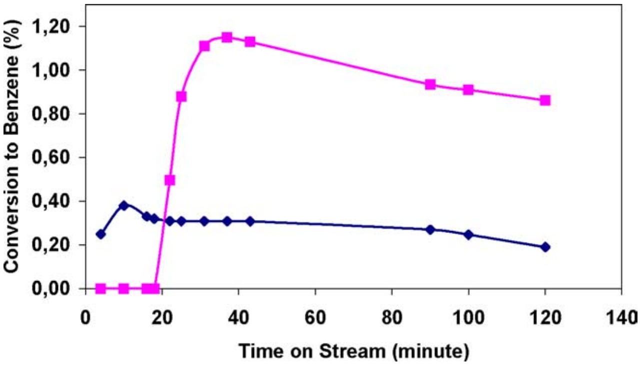

Fig. 1. Variation of the conversion to benzene with time on stream for (◆) the carburized catalyst with a 24:736 CH_4:Ar mixture at a flow rate of 13 L/h at 700 °C, and (■) the nonprecarburized catalyst with a 380:380 CH_4:Ar mixture at a flow rate of 0.75 L/h at 700 °C.

be molybdenum carbidic species, operate right away for the conversion of methane, while in the HP experiment the active centers are to be formed during the induction period. This is clearly evident from the comparison of curves given in Fig. 1, which shows the variation of the conversion with time on stream. The next obvious observation was the much higher conversion in the case of the HP experiment. The latter conversion level was within three times the one achieved in the LP experiment. In addition, the shapes of the curves representing the conversion as a function of time on stream were quite different for the two experiments. Not only the induction period was absent in the case of the LP experiment, but also conversion was observed to peak to a maximum and decay swiftly during the early period and then slowly decrease during the next hour. By contrast in the HP experiment, after the induction period, an abrupt rise in conversion was observed followed by a rapid decay. The rate of decrease of the activity of the catalyst operating under the HP conditions appears to be more steady and higher than that observed under the LP conditions following the early decay consecutive to the initial peak.

As far as the product distribution is concerned, as expected, no other aromatic but benzene was observed in the early period of the LP experiment together with 10% ethylene. Later, within 2 h, increasing amounts of ethylene were produced, along with trace amounts of naphthalene, as shown in Fig. 2. By contrast, in the HP experiment, all products appeared simultaneously following the induction period, as shown in Fig. 3. They included ethylene, ethane, benzene, and naphthalene. This is reasonable since the low pressures prevent sequential reactions to produce the end products, while at higher pressures more end products are to be expected.

These results illustrate the overriding influence of the methane pressure both on the rate of reaction and on the product distribution.

Most of these observations are in agreement with earlier results, particularly those reported by Iglesia and coworkers. [21]. They indicate that the rate of decay is related to the formation of increasingly heavier products and suggest, as has been already proposed [13,14,18,19], that ethylene is a likely primary product or at least the very first secondary product of methane conversion.

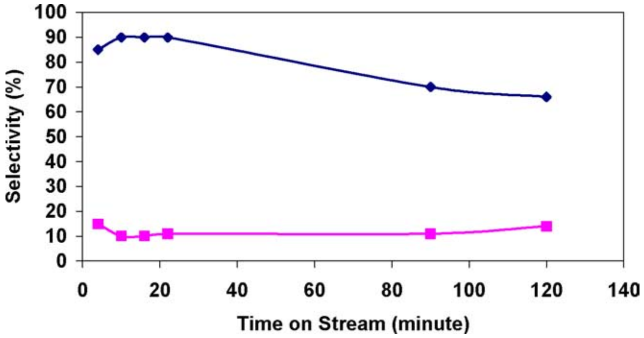

Fig. 2. The product distribution after the reaction under low-pressure experimental conditions, namely with a 24:736 CH_4:Ar mixture at a flow rate of 13 L/h at 700 °C. (◆) Benzene; (■) ethylene.

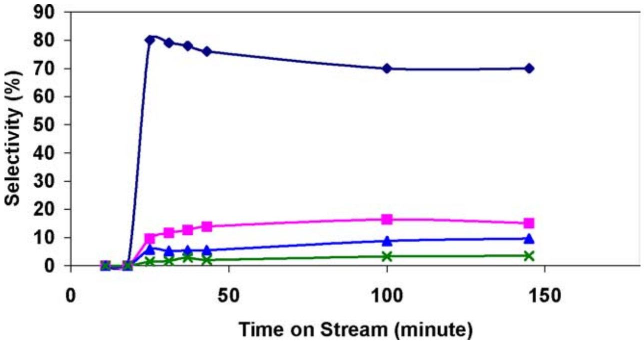

Fig. 3. The product distribution after the reaction under high-pressure experimental conditions, namely with a 380:380 CH_4:Ar mixture at a flow rate of 0.75 L/h at 700 °C. (◆) Benzene; (■) ethylene; (▲) ethane; (×) naphthalene.

In the HP experiments, in agreement with Iglesia and co-workers [21], surface dealumination produced, in every respect, similar results to those observed by them in the case of silanation. Indeed, molybdenum supported over the dealuminated zeolite exhibited a higher stability with time on stream (Fig. 4). This is quite reasonable since, as already suggested, active centers on the external surfaces including the surface carbidic species and the surface acid sites would contribute to the formation of the end products which are the bulkiest and the least amenable to desorption, thus resulting in activity decay. However, it is less conceivable that the activity increased with decreasing number of active sites. Yet, we observed the same result.

However, the results obtained under the LP conditions are at variance with those obtained under the HP conditions. As expected, the association of molybdenum with the dealuminated zeolite has brought about a better stability, particularly after a period of 2 h on stream. In addition, the data also showed that the dealuminated zeolite associated with Mo was less active than the parent zeolite. The activity was about half of that exhibited by molybdenum over the unmodified

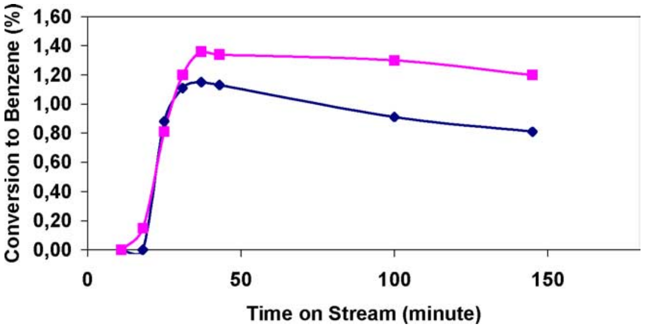

Fig. 4. Variation of the conversion to benzene with time on stream under HP conditions for (◆) the original catalyst without dealumination with a 380:380 CH_4:Ar mixture at a flow rate of 0.75 L/h at 700 °C, and (■) the catalyst dealuminated with oxalic acid with a 380:380 CH_4:Ar mixture at a flow rate of 0.75 L/h at 700 °C.

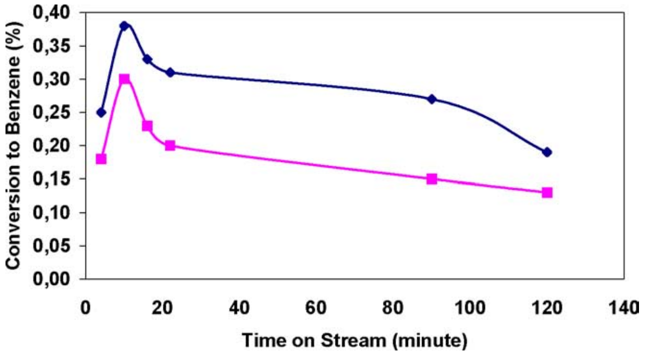

Fig. 5. Variation of the conversion to benzene with time on stream under LP conditions for (◆) the original catalyst without dealumination, with a 24:736 CH_4:Ar mixture at a flow rate of 13 L/h at 700 °C, and (■) the catalyst dealuminated with oxalic acid, with a 24:736 CH_4:Ar mixture at a flow rate of 13 L/h at 700 °C.

zeolite, which may be indicative of the effective decrease of the total number of active sites. This is clearly seen from Fig. 5 and is in agreement with the results reported recently by Tang et al. [33] who found that the association of molybdenum with a ZSM-5 of a Si/Al ratio of 20 was more active than with the ZSM-5 dealuminated with HCl to a Si/Al ratio of 50 prior to its association with Mo.

This might mean, contrary to the claim of Iglesia and co-workers, that suppression of the external surface sites does not improve the dispersion of the molybdenum precursor if it is accepted that the acid sites are the anchoring centers of the molybdenum active species. In this case it appears, rather, that the number of such active sites has, actually, decreased or at least their efficiency did. It is even conceivable to measure the ratio of the active internal to external sites. However this is contradicted by the results obtained under higher methane pressure, well in agreement with those obtained by Iglesia and co-workers.

We therefore suggest that, under reduced methane pressure, as is obvious from the product distribution, the sequence of the reaction is quenched to its early stages because of the lower conversion due both to the low methane pressure that lowers the reaction rate and to the high space velocity that lowers the residence time and hence the conversion. Therefore the heaviest products which are, if not the poisons, at least the poison precursors, are produced in much lower yields and deactivation is still not dramatic in the early stages of analysis. Hence, the conversions and rates determined under these circumstances closely approach the actual rates or are only slightly undermined by the starting deactivation. Thus it is conceivable that the catalyst associated with the dealuminated HZSM-5 should show the lowest activity under these conditions.

By contrast, under higher methane partial pressure and decreased space velocity, the sequence of reactions should produce, as was observed, higher molecular weight aromatics. The early analyses are probably already altered by deactivation. If this were true, it is expected, as Iglesia and co-workers have proposed, that the catalyst associated with the externally dealuminated HZSM-5 should not be so dramatically altered by the starting deactivation as the one associated with the unmodified zeolite. Therefore it would exhibit an apparently higher activity solely in view of a less advanced deactivation on the external surfaces, hence easier access to the internal surfaces, and probably not because it contains more active sites than the untreated catalyst. Also, it could be envisaged that since dealumination is mainly concerned with the external sites, the formation of the heavier products which need free space is no longer favored. Therefore, statistically, the stability against coking of such catalysts should be improved, resulting in apparent improvement of the overall activity under particular circumstances.

This reconciles the fact that at the lowest conversion, under conditions where both catalysts are the least affected by deactivation, the order of activity is just the opposite depending on the reaction conditions.

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