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The effect of CaC_2 on the activity of MFI-supported molybdenum catalysts for the aromatization of methane

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Abstract

The effect of CaC_2 on the activity of MFI-supported molybdenum catalysts was investigated in the dehydrocyclization of methane. Treatment with CaC_2 enhanced the activities of the catalysts in comparison to the activities of those which were not precarburized or prepared by precarburization with a CH_4/H_2 mixture. The induction period seen in the case of the sample prepared without precarburization decreased with CaC_2 treatment. CaC_2 loading above a certain value, however, gave poor results, possibly due to pore blockage in the support. All samples, precarburized with CaC_2 or CH_4/H_2 mixture or carburized in the course of the reaction, deactivated in a similar manner after the variable induction period.

Keywords: Methane; Dehydrocyclization; CaC_2; MFI; Molybdenum; Precarburization

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 catalyst precursors. 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 showed 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 [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 naphthalene was the most frequently noted, although mole-

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cules 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].

The present study was conducted to see if carburization might be possible in the presence of CaC_2 as the carburization agent. We have impregnated the catalyst support, namely HZSM-5, with ammonium molybdate and treated the catalysts with various amounts of CaC_2 under an argon atmosphere at 700 °C. The activities of the catalysts, which are believed to be carburized in the presence of CaC_2, were compared with those of the catalysts, one of which was not precarburized and the other was carburized with a CH_4/H_2 mixture as was routinely carried out in the previous studies.

2. Experimental

Wet impregnation method was used to prepare the catalysts. Ammonium molybdate ($(NH_4)_2MoO_4$, Touzart & Matignon) was dissolved in a minimum volume of water and HZSM-5 ($Si/Al = 28$, Sud Chemie, Germany) was added to the solution so as to achieve a nominal molybdenum content of 4% by weight. Chemical analysis confirmed the molybdenum content to be 3.85%. The slurry was subsequently dried at 80 °C. A 300-mg sample of the dry powder was placed in a U-shaped quartz reactor with 14 mm inner diameter and was first activated in dry air at 650 °C and then purged by argon flow (Air Liquide UP) at the same temperature, for 30 min.

For precarburization in the presence of CH_4 and H_2, a gas mixture with a CH_4/H_2 ratio of 0.42:10.2 (both in L/h^{-1}) was flown over the catalyst bed for 5 h at a temperature of 700 °C. After the precarburization step, the catalyst bed was purged with argon at the same temperature for 30 min. Methane conversion was also carried out at 700 °C using 0.42 L/h methane diluted with argon in order to obtain a total flow rate of 13 L/h, resulting in a methane partial pressure of about 24.6 Torr in the CH_4/argon mixture.

For precarburization with CaC_2, a 300-mg sample of Mo/HZSM-5 (4 wt% Mo), after being activated in dry air at 650 °C, was cooled to room temperature under argon atmosphere. At room temperature, CaC_2 (4, 8, 16, 24, and 32 mg) was added to the sample and was then mechanically mixed thoroughly with the sample under argon atmosphere. The CaC_2–Mo/HZSM5 mixture was subsequently heated to 700 °C under argon atmosphere. XRD analyses showed that the MFI structure suffered no damage from either the CH_4/H_2 or the CaC_2 treatments. The CH_4/argon mixture was then fed to the reactor for the test reaction. As usual, the reaction mixture consisted of 0.42 L/h CH_4 in the diluent gas, argon, and the total flow rate of the CH_4/argon mixture was adjusted to 13 L/h.

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 maximum sensitivity under optimal separation conditions was within 1–5 nmol. 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. The maximum sensitivity was within 50 nmol.

The rate of CH_4 conversion to hydrocarbons (benzene, naphthalene, and ethylene) in mol $CH_4/(s\,mol_{Mo})$ was calculated from the following equation

$$r_{HC} = F_{CH_4,inlet} X_{CH_4\,to\,HC} (1/n_{Mo}), \tag{1}$$

where $F_{CH_4,inlet}$ is the total inlet molar flow rate of CH_4 in mol/s, $X_{CH_4\,to\,HC}$ is the CH_4 conversion to hydrocarbon products, namely benzene, naphthalene, and ethylene, and n_{Mo} is the number of moles of molybdenum atoms present on the catalyst sample. CH_4 conversion to hydrocarbon products ($X_{CH_4\,to\,HC}$) was calculated from the partial pressures of the hydrocarbons formed based on the measured GC responses, reaction stoichiometries, and the differential reactor assumption, as $P_{CH_4\,to\,HC}/P_{CH4,inlet}$.

For quantitative evaluation of coke formation, the rate of CH_4 conversion to coke (mol $CH_4/(s\,mol_{Mo})$) was calculated from the following equation

$$r_{coke} = F_{CH_4,inlet} X_{CH_4\,to\,coke} (1/n_{Mo}), \tag{2}$$

where $X_{CH_4\,to\,coke}$ is the CH_4 conversion to coke. CH_4 conversion to coke was derived from the measured total H_2 formed 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 by assuming that coke formation was due to the simple decomposition of CH_4 into C and H_2.

Selectivity to any hydrocarbon product was defined as the ratio of the CH_4 converted to that product to the total CH_4 converted to hydrocarbon products.

3. Results and discussion

As seen in Fig. 1, the highest rate of formation of hydrocarbon products (benzene, naphthalene, and ethylene) was obtained when the 300-mg catalyst sample was treated with 4 mg CaC_2. Heating the catalyst in the presence of CaC_2 resulted in about a 40% higher value for the maximum rate of hydrocarbon formation, when compared to the maximum rate values obtained with the other two catalysts, one of which was not precarburized and the other was carburized with a CH_4/H_2 mixture prior to the reaction. A maximum conversion of methane into hydrocarbons of about 1.7% was

Table 1
Maximum rates of hydrocarbon and coke formation, and the corresponding reaction times

Sample	Hydrocarbon products		Coke	
	Reaction time (min)	Max. rate ($\times 10^{-3}$ mol/(mol$_{Mo}$ s))	Reaction time (min)	Max. rate ($\times 10^{-3}$ mol/(mol$_{Mo}$ s))
Noncarburized	40	0.654	28	7.97
Precarburized	16	0.652	10	4.84
4 mg CaC_2	22	0.918	16	9.31
8 mg CaC_2	28	0.870	16	9.42
16 mg CaC_2	28	0.801	16	8.49
24 mg CaC_2	28	1.006	16	8.58
32 mg CaC_2	40	0.589	22	9.78

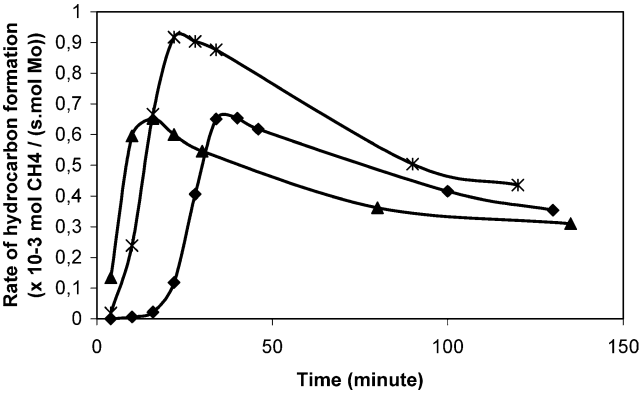

Fig. 1. Variation of the rate of hydrocarbon formation with time for the samples, which were (◆) noncarburized, (▲) precarburized in the presence of CH_4/H_2 mixture, and (∗) treated with 4 mg CaC_2.

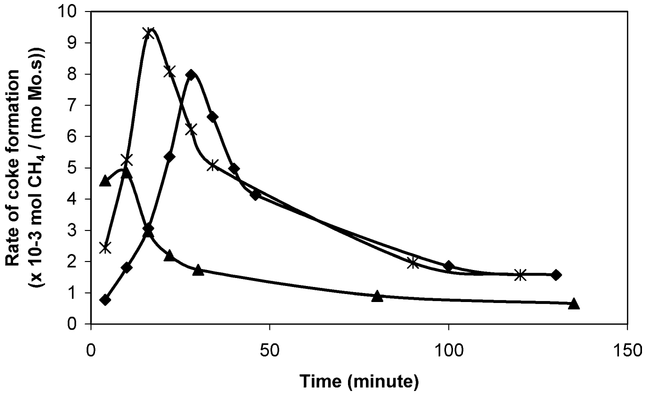

Fig. 2. Variation of the rate of coke formation with time for the samples, which were (◆) noncarburized, (▲) precarburized in the presence of CH_4/H_2 mixture, and (∗) treated with 4 mg CaC_2.

achieved with these latter two catalysts, which increased to about 2.4% with 4 mg CaC_2 addition. Conversion into hydrocarbons leveled off for all samples to below 1%, over 2 h on stream. It is apparent from Fig. 1, that the induction period, defined as the time necessary to detect methane conversion products was consistently shortened, if at all present. In addition, the period of time on stream needed to achieve maximum rates, t_{max}, was also significantly reduced (Fig. 1, Table 1) upon treatment with CaC_2, when compared to the noncarburized catalyst. For example, the maximum rate was reached within 22 min over the sample pretreated with 4 mg CaC_2, whereas it was reached after 40 min for the noncarburized sample and after only 16 min for the sample precarburized with CH_4/H_2 mixture. It is clear that formation of Mo_2C, assumed to be the active species, had taken place to a significant extent via the carburization of the MoO_3 species, prior to the reaction period upon treatment with CaC_2.

It is apparent from the induction period and t_{max} values that precarburization of the sample with CH_4/H_2 mixture was almost completed before the reaction started to take place under a CH_4/argon mixture. Likewise, a significant degree of carburization was also observed to take place prior to the reaction period for the sample treated with 4 mg CaC_2, as evidenced by the drastic reduction of the induction period by comparison with untreated samples and by the shorter t_{max}. For this sample, carburization was seen to continue to some extent during the course of the reaction too, although no CO_x evolution was observed under flowing methane.

In Fig. 2, the variation of the rate of coke formation with time on stream is shown for the same samples. As can be seen from the figure, coking was lowest for the sample precarburized with the CH_4/H_2 mixture, and highest for the one treated with 4 mg CaC_2. The corresponding values of maximum conversion of methane into carbon and hydrogen were about 12.5% for the sample precarburized with CH_4/H_2 mixture, 20.6% for the sample used without precarburization, and 24% for the sample treated with 4 mg CaC_2. Conversion values leveled off for all samples to below 5% over 2 h on stream. The sample with the highest activity for the aromatization reaction also showed the highest activity for coking.

Table 1 shows that the maximum rate of coke formation was obtained within 16 min for the sample pretreated with 4 mg CaC_2, whereas the maximum rate of hydrocarbon formation was obtained within 22 min for the same sample. The maximum rates of coke and hydrocarbon formation for the noncarburized sample were obtained within 28 and 40 min, respectively. The same values were 10 and 16 min, respectively, for the sample precarburized in the presence of the CH_4/H_2 gas mixture.

For all samples, maximum rates of coke formation had been reached before the maximum level of rate values for the secondary products was attained. Neither precarburization in the presence of the CH_4/H_2 mixture nor that with CaC_2

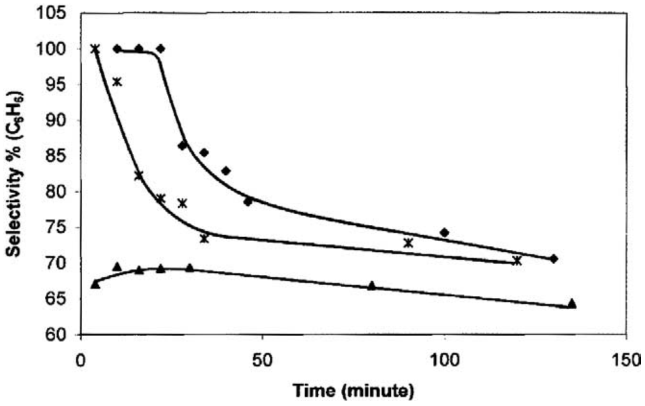

Fig. 3. Variation of the selectivity (%) for C_6H_6 with time for the samples, which were (◆) noncarburized, (▲) precarburized in the presence of CH_4/H_2 mixture, and (∗) treated with 4 mg CaC_2.

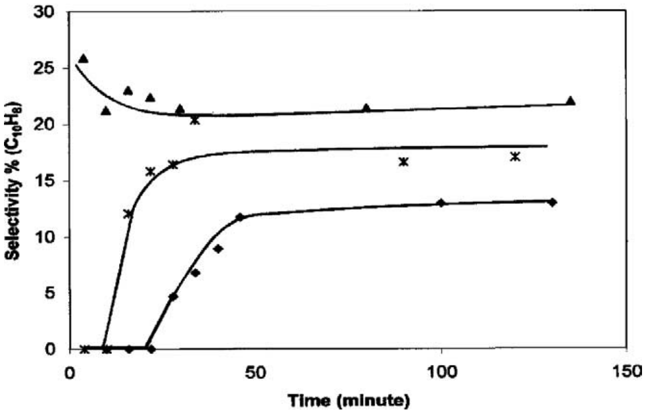

Fig. 4. Variation of the selectivity (%) for $C_{10}H_8$ with time for the samples, which were (◆) noncarburized, (▲) precarburized in the presence of CH_4/H_2 mixture, and (∗) treated with 4 mg CaC_2.

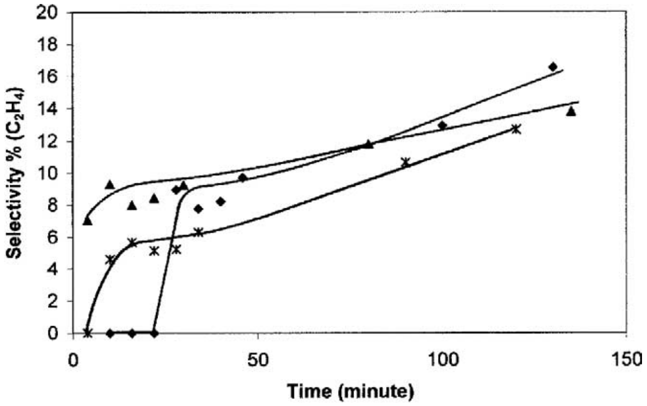

Fig. 5. Variation of the selectivity (%) for C_2H_4 with time for the samples, which were (◆) noncarburized, (▲) precarburized in the presence of CH_4/H_2 mixture, and (∗) treated with 4 mg CaC_2.

were effective in postponing or depressing coking reactions till after the formation of the aromatization products. Coking seems to be taking place in parallel and slightly but consistently preceding the aromatization reactions in all cases. This latter observation that the maximum coke yield was reached before the maximum yield of secondary reaction products was attained supports the claim of Lunsford and coworkers [13] and Iglesia and co-workers [33], regarding the possible function of coke in promoting the reaction during the initial periods. Indeed, if it is assumed that dimolybdenum carbide is the active precursor for methane conversion into a C2 primary compound (ethylene or acetylene), one might speculate, in agreement with Lunsford and coworkers [13] and Iglesia and co-workers [33], that methane decomposition into carbon and hydrogen would convert the overactive dimolybdenum carbide into the truly active carbide capable of generating C–C bonds upon interaction with methane. However, at this time, it is not clear why the initial rate of conversion of methane into the secondary products is zero, for the sample precarburized with calcium carbide, in contrast to the sample precarburized with the CH_4/H_2 mixture. We may only speculate that cleaning of the molybdenum carbide from excess calcium carbide by the hydrogen issued from the methane decomposition into its elements is a prerequisite to the formation of the hydrocarbons or to the formation of the actual active carbide species.

In Figs. 3, 4, and 5, the selectivities versus time on stream for benzene, naphthalene and ethylene, respectively, are shown. In the case of the sample treated with 4 mg CaC_2, 100% benzene selectivity was obtained as a result of the initial analysis carried out 4 min after the reaction was started. Later, ethylene and then naphthalene were detected, after 10 and 16 min, respectively. No acetylene was detected, although it is likely to be the primary product. This is easily conceivable in the presence of an exceedingly high pressure of hydrogen compared to the potential pressure of acetylene. The initial selectivity to benzene, 100%, among aromatics, is only indicative that the reaction mixture is off the thermodynamic equilibrium as long as benzene may easily escape the reaction pot.

For the noncarburized sample, no reaction product except hydrogen could be measured initially. Benzene was the only other product detected besides hydrogen, during the period between 10 and 22 min. After this time, both naphthalene and ethylene were observed in the product mixture. This occurrence is very interesting. It seems to be indicative of three distinct processes: the exclusive evolution of hydrogen may suggest that the oxidic molybdenum was being activated not only into the dimolybdenum carbide but probably into yet another intermediate surface carbide capable of creating C–C bonds in a first step, followed by a second period, during which only benzene was detected, corresponding to the quantitative conversion of the intermediate ethylene (acetylene) into benzene, presumably over the fresh acid sites or appropriate ensembles of the carbide itself. The high rate of conversion of the intermediate ethylene/acetylene must have been secured since no deactivation of the acid sites had yet occurred. In the third period corresponding to the accumulation of benzene together with the C2 precursor leading to multiple alkylations of the former, a deposit of heavier

Table 2
Values of the $C_6H_6/C_{10}H_8$ ratios, the times that ethylene selectivities started increasing, and the times that naphthalene was first detected in the product mixture

Sample	$C_6H_6/C_{10}H_8$ ratios	The times that ethylene selectivities start increasing	The times that naphthalene was first detected in the product mixture
Noncarburized	9.3	34	28
Precarburized	3	16	4
4 mg CaC_2	5	22	16
8 mg CaC_2	7.9	28	22
16 mg CaC_2	8.7	22	16
24 mg CaC_2	6.8	28	16
32 mg CaC	8.8	28	28

aromatics must have formed that hindered the quantitative conversion of the primary product, which then started to be detected as well. With time on stream, formation of increasing amounts of heavy aromatics would inhibit the conversion of the primary product leading to an increased selectivity for the latter, despite a decrease in the overall methane conversion rate. By contrast, all three reaction products were detected to start forming within the first 4 min when the sample precarburized in the presence of CH_4/H_2 gas mixture was used as the catalyst.

Selectivities for ethylene, following its formation, initially increased quite rapidly and then, following a limited depression period, continued to increase steadily at a slower rate. It is evident that the ethylene/acetylene intermediate is produced at the highest possible rate when all potential production sites are present, as in the case of the precarburized samples at early times. Conversion of the primary intermediate into benzene is accompanied, due to the high rate of C2 production, by the formation of higher aromatics as well, resulting in significant consumption of ethylene/acetylene and consequently in an apparent depression of the ethylene selectivity. As heavier aromatics are accumulating, deactivation of the function in charge of ethylene conversion is progressively taking place; hence increasing ethylene selectivities are observed again with time on stream. Table 2 gives the times that ethylene selectivities started increasing after the depression period, and the times that naphthalene was first detected in the product mixture. The sample precarburized with CH_4/H_2 gas mixture is seen to have been exposed to deactivation earlier than the other two samples. The sequence of the deactivation stages seems to be related to the degree of carburization that has taken place prior to the reaction. The lower the degree of carburization, as indicated by the longer induction period and longer $t_{\max}$ values, the later the deactivation took place, as evidenced by the lack of naphthalene and ethylene in the product mixture. The catalyst pretreated with CaC_2, therefore, started to be deactivated earlier than the noncarburized sample. On the other hand, deactivation took place, in any case, sooner or later with time on stream for all samples, irrespective of the activation method.

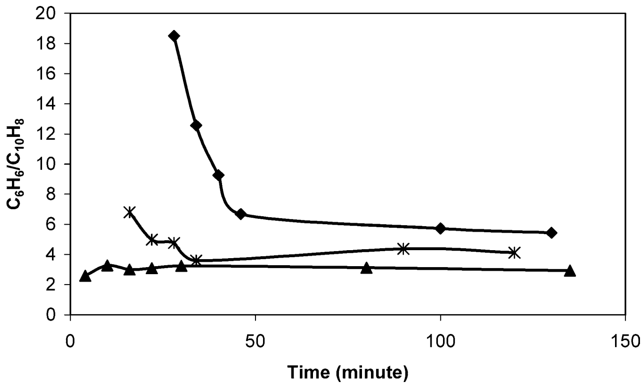

Fig. 6. Variation of the $C_6H_6/C_{10}H_8$ ratio with time for the samples, which were (◆) noncarburized, (▲) precarburized in the presence of CH_4/H_2 mixture, and (∗) treated with 4 mg CaC_2.

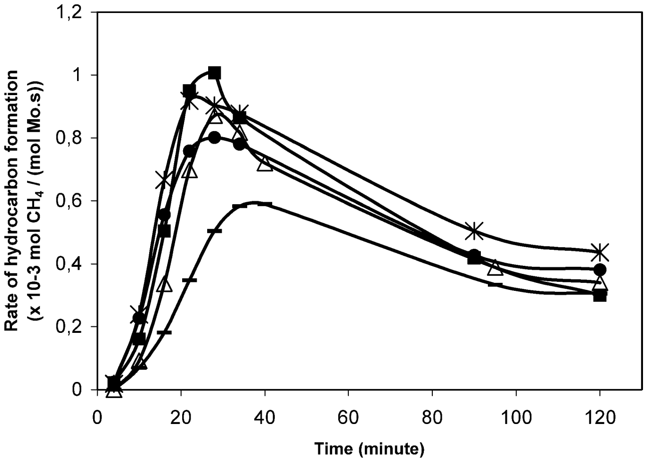

Fig. 7. Variation of the rate of hydrocarbon formation with time for the samples, which were treated with (∗) 4 mg CaC_2, (△) 8 mg CaC_2, (●) 16 mg CaC_2, (■) 24 mg CaC_2, and (–) 32 mg CaC_2.

Fig. 6 shows the variation of the benzene to naphthalene ratios with respect to time for the samples. The values of these ratios at the highest conversion levels for the secondary products are also given separately, in Table 2. Benzene to naphthalene ratio was 9.3 for the noncarburized sample, 5 for the sample pretreated with 4 mg CaC_2, and 3 for the sample precarburized with CH_4/H_2 mixture. The higher the ratio, the lower the extent of the deactivation, as expected from the reaction sequence, since naphthalene may be derived from divinylbenzene formed by alkylation of benzene with acetylene and is considered as the coke precursor.

Fig. 7 shows the rate of hydrocarbon formation with respect to time for the samples treated with various amounts of CaC_2, namely 4, 8, 16, 24, and 32 mg. The maximum values and the times at which these rates were attained are also given in Table 1. Higher rates of hydrocarbon formation were observed for all of these samples, except for the sample treated with 32 mg CaC_2, when compared to the noncarburized sample and the sample precarburized with CH_4/H_2 mixture. Besides having the lowest rate of hydrocarbon formation, the sample treated with 32 mg CaC_2 also gave a

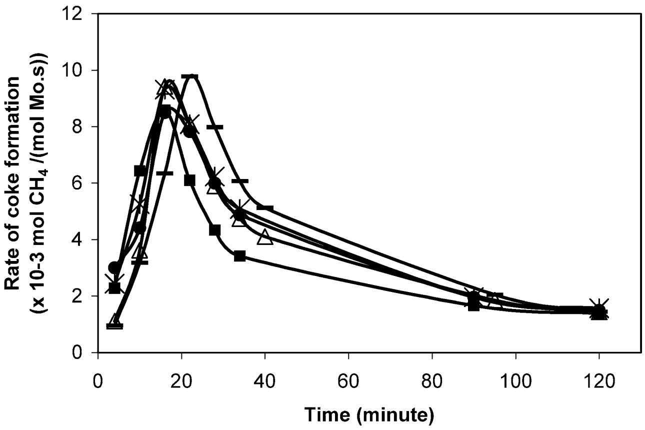

Fig. 8. Variation of the rate of coke formation with time for the samples, which were treated with (∗) 4 mg CaC_2, (△) 8 mg CaC_2, (●) 16 mg CaC_2, (■) 24 mg CaC_2, and (–) 32 mg CaC_2.

t_{max} value which was significantly longer than those of the other samples treated with CaC_2, similar to the noncarburized sample, as seen from Table 1, although, contrary to the case of noncarburized sample, significant amounts of hydrocarbons were detected at the early reaction times with this sample, yet in small yields. The time that naphthalene has first formed as the secondary product was 28 min for this sample, which is the same as the respective time obtained for the noncarburized sample (Table 2). On the other hand, the rate of coke formation does not seem to vary significantly with the amount of CaC_2; even the value obtained for the sample treated with 32 mg CaC_2 is similar to those of the other catalysts, as seen in Fig. 8.

The lower rate observed for the sample treated with 32 mg CaC_2 may be due to restricted diffusion into the zeolite framework due to pore blockage by CaC_2. As noted above, the shorter t_{max} values and the quasi suppression of the induction periods observed for the samples treated with CaC_2 in comparison to the noncarburized sample are expected to be related to the possible Mo_2C formation from CaC_2 and MoO_3 or $MoO_2{}^{2+}$ in accordance with either of the following two reactions:

$$10MoO_3 + 8CaC_2 \rightarrow 5Mo_2C + 8CaO + 11CO_2, \tag{3}$$

$$6MoO_2{}^{2+} + 7CaC_2 \rightarrow 3Mo_2C + 6Ca^{2+} + CaO + 11CO. \tag{4}$$

It is well known from the previous studies that after impregnating HZSM-5 with ammonium molybdate ($(NH_4)_2MoO_4$), MoO_3 clusters are formed on the external surfaces of HZSM-5 [18,28]. After heating the sample to 650 °C under oxygen atmosphere, $(MoO_2)^{2+}$ or $(Mo_2O_5)^{2+}$ species form and migrate in the zeolite framework to replace the H^+ ions. These species are further converted into Mo_2C by reaction with methane.

In the case of the treatment with CaC_2, on the other hand, CaC_2 reacts with the MoO_x species. As to how carburization of the molybdic species may occur, it may be conceived that calcium carbide ($a = 5.92$ Å) might diffuse at 700 °C into the MFI channels ($D = 5.5$ Å); alternatively, Ca^{2+} ions may migrate to exchange progressively with the cationic molybdic entities, which then are carburized. The decrease in the activity observed for the sample treated with 32 mg CaC_2 may be due to restricted diffusion, as noted above, into the zeolite framework due to pore blockage by CaC_2. Pore blockage due to excess amount of CaC_2 may be gaining importance at relatively high amounts of loading since higher rates of hydrocarbon formation were obtained for the catalyst samples treated with CaC_2 at the amounts of 4, 8, 16, and 24 mg, but not with 32 mg. The higher activities may be related to the Mo_2C cluster sizes formed after reaction. As claimed by Iglesia and co-workers [24], stronger interactions of CH_x fragments with nanoclusters of molybdenum carbides than with bulk carbide surfaces may be prevailing because of higher coordinative unsaturation of Mo centers in such small clusters [24]. In the case of the treatment with CaC_2, CaC_2 may only react with $(MoO_2)^{2+}$ or $(Mo_2O_5)^{2+}$ species, instead of bulk MoO_3, and hence more stable Mo_2C species to agglomeration may be formed at the H^+ sites in the zeolite framework. Higher dispersion of Mo_2C species in the zeolite framework by preferential reaction of CaC_2 with $(MoO_2)^{2+}$ or $(Mo_2O_5)^{2+}$ species may be the reason for the higher activities in the activation of CH_4, observed for the catalysts carburized with CaC_2 in comparison to the other samples, noncarburized or precarburized with a CH_4/H_2 mixture.

Although methane conversion rates were within 1 mmol/mol Mo.s and therefore less than half of the rates observed in the literature and in particular by Derouane and co-workers [29,30], it is worth noting that the methane pressure used here was about 30 times less than by the latter reports. Assuming a first-order rate law with respect to methane is more than enough to account for the lower rates we did observe. In fact, Vu Thu Ha [34] has shown that the order with respect to methane of the reaction rate was 1.26 in the 300–760 Torr pressure range.

4. Conclusions

It was shown that it is possible to precarburize MoO_3/HZSM-5 catalyst samples to a considerable extent prior to the aromatization reaction by treatment with CaC_2. Higher activities were obtained for these catalysts in comparison to the samples noncarburized or precarburized in the presence of CH_4/H_2 mixture. The higher dispersion of Mo_2C species in the zeolite framework by preferred reaction of CaC_2 with $(MoO_2)^{2+}$ or $(Mo_2O_5)^{2+}$ species was proposed as a plausible explanation for the higher activities. On the other hand, deactivation was observed to take place in a similar manner after the induction period in parallel to the desired reaction sequence leading to benzene formation, for all samples, independent of the method of activation.

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