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Combined single-pass conversion of methane via oxidative coupling and dehydro-aromatization

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A single-pass process with the combination of oxidative coupling (OCM) and dehydro-aromatization (MDA) for the direct conversion of methane is carried out. With the assistance of the OCM reaction over the $SrO–La_2O_3/CaO$ catalyst loaded on top of the catalyst bed, the duration of the dehydro-aromatization reaction catalyzed by a 6Mo/HMCM-49 catalyst shows a significant improvement, and. the initial deactivation rate constant of the overall process revealed about 1.5×10^{-6} s^{-1}. Up to 72 h on stream, the yield of aromatics was still maintained at 5.0% with a methane conversion of 9.6%, which is obviously higher than that reported for the conventional MDA process with single catalyst. Upon the TPR results, this wonderful enhancement would be attributed to an in-situ formation of CO_2 and H_2O through the OCM reaction, which serves as a scavenger for actively removing the coke formed during the MDA reaction via a reverse Boudouard reaction and the water gas reaction as well.

KEY WORDS: combined conversion of methane; oxidative coupling; dehydroaromatization; 6Mo/HMCM-49.

1. Introduction

Recently, methane dehydro-aromatization (MDA) over Mo/HZSM-5 under non-oxidative conditions has received considerable attention [1–4]. To obtain higher yield of aromatics (especially benzene) and hydrogen the temperature of the MDA reaction usually proceeds at 973 to 1073 K. Fast deactivation of the catalyst due to coke formation is a challenge for its industrial application. Modification of the catalyst, e.g. introduction of second transition metal ions [5], dealumination of framework A1 [6–8] and silanation of the outer surface [9] of HZSM-5, as well as post-steam-treatment of the Mo/HZSM-5 catalysts [10,11], have been studied to improve the catalytic reaction performance of the MDA reaction.

Different zeolite-based Mo catalysts have also been extensively tested. It was reported that in comparison with the Mo/HZSM-5 catalyst, the Mo/HMCM-22 catalyst showed better catalytic performance at 973 K with the selectivity to benzene of 80% at a methane conversion of 10% [12]. Recently, MoO_3 supported on nano-sized HMCM-49 has also been reported, with aromatics yields of about 10% at 973 K. This was achieved for 150 h with several regenerations by air and addition of MoO_3 in between [13].

Addition of a proper amount of CO_2, H_2, or H_2O into the methane feed is another effective means to prolong the lifetime of the Mo-based zeolite catalyst [14–20]. Based on these discoveries, we have found a new combined single-pass conversion of methane via oxidative coupling on $SrO–La_2O_3/CaO$ (SLC) or La_2O_3/BaO (LB) and dehydroaromatization on 6Mo/HZSM-5 [21,22] catalyst system that appears highly effective. By means of the formation of CO_2 and H_2O in the top layer of the reactor over the SLC or LB catalyst, the catalytic performance of the MDA reaction in the second layer over the Mo/HZSM-5 catalyst is greatly improved. The aromatics yield was 5.0% after 30 h on stream at a methane conversion of ca. 12.0%.

In our new work, the combined single-pass conversion of methane via oxidative coupling and dehydro-aromatization was carried out on an SLC-6Mo/HMCM-49 catalyst system. The aromatics yield is now 5.0% after 72 h on stream at a methane conversion of 9.6%. Detailed analysis of the carbonaceous deposits on the 6Mo/HMCM-49 at different durations of time on stream showed two peaks in the corresponding TPO profiles. It was concluded that if CO_2 and H_2O components were put simultaneously into the CH_4 feed, both of them will play roles in elimination of carbonaceous deposits formed on the 6Mo/HMCM-49 catalysts.

2. Experimental

HMCM-49 zeolite was supplied by Jilin University and synthesized according to the hydrothermal procedures by using hexamethyleneimine (HMF) as a template and silica gel as the silicon source [23]. The

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synthesized sample was dried, calcined and exchanged with NH_4NO_3. The HMCM-49 zeolite was impregnated with ammonium heptamolybdate for 24 h at room temperature, and then dried for 3 h at 393 K, followed by calcination in static air at 773 K for 6 h [24,25]. In this work, the Mo content in the Mo/HMCM-49 catalysts was 6 %(wt) and hereafter, for brevity, it is denoted as 6Mo/HMCM-49 in the context.

The 20 wt% SrO–20 wt%La_2O_3/CaO (SLC) catalysts were prepared by a co-precipitation method. A $(NH_4)_2CO_3$ solution was dropped in a mixed solution of Sr, La and Ca nitrates in a desired ratio, and then left overnight. It was then dried and calcined at 1073 K for 4 h. The sample was ground, tableted, crushed and sieved to 20–40 mesh and stored in a desiccator before use.

When only the 6Mo/HMCM-49 catalysts were evaluated, the catalytic test was carried out at atmospheric pressure and a temperature of 983 K. The charge of the 6Mo/HMCM-49 catalysts was 0.35 g. The catalysts were first heated under a He stream to the reaction temperature, and then the reactant gases were introduced into the reactor. The space velocity of CH_4/N_2 (CH_4:N_2 = 9:1) was fixed at 1500 ml/g/h. The tail gas was analyzed by a Varian 3800 online gas chromatograph, which was equipped with a flame ionization detector (FID) for the analysis of CH_4, C_6H_6, C_7H_8, $C_{10}H_8$ and a thermal conductivity detector (TCD) for the analysis of H_2, N_2, CH_4, CO, C_2H_4, C_2H_6. About 10% N_2 in the feed was used as an internal standard for the analysis of all products, including coke deposition, as suggested by Wang *et al.* [26].

In our initial studies on the combined single-pass conversion of CH_4 via oxidative coupling and dehydroaromatization, we found that the reaction conditions are critical in allowing the desired OCM and MDA reactions to proceed concertedly and effectively [21,22]. The SLC catalyst was put in the top layer and the 6Mo/HMCM-49 in the second layer in a quartz tubular fixed-bed reactor. The charge of the SLC catalyst was 0.05 g and that of the 6Mo/HMCM-49 catalysts was 0.35 g. In this work, a ratio of O_2 to CH_4 of about 0.6:100 (in volume) was finally selected and the reaction temperature was set at about 983 K. The catalysts were first heated under a He stream to the reaction temperature, and then the reactant gases were introduced into the reactor. The space velocity was fixed to be 1581 ml/g/h with the ratio of O_2: (N_2 + He):CH_4 = 0.6:16.5:100.

After running the reaction for 5, 21 and 62 h, the coke deposited on the 6Mo/HMCM-49 catalyst was analyzed by TGA and TPO. The TGA was carried out on a Perkin–Elmer Pyric Dimond TG/TDA instrument. About 15 mg of the coked sample was loaded and then heated from room temperature (r.t.) to 1073 K at a heating rate of 10 K/min in an air stream (100 ml/min). The TPO was carried out using an online quadruple mass spectrometer (Balzers, QMS 200). About 50 mg of coked catalyst was charged in a U-shape quartz tube. The sample was heated to 873 K and kept at this temperature for 30 min in a He stream (30 ml/min) to remove adsorbed water. After cooling to r.t. in the He stream, the sample was flushed with a 10% O_2/He mixture (50 ml/min) at room temperature for 30 min. The temperature was raised from 303 K to 1023 K at a heating rate of 8 K/min during which the signal intensity of m/e = 44(CO_2) and 28(CO) were recorded. The CO_2 and CO signals were calibrated by thermal decomposition of different weights of $Cu(CO_3)\cdot Cu(OH)_2$. A fragment of CO_2 which contributed to the signal of m/e = 28(CO) was subtracted according to standard weight peaks of mass spectrometer from the total intensity at m/e = 28(CO) to get the real amount of CO. The total signal intensity of carbonaceous deposits should be the summation of the corrected peak areas of CO and CO_2. The total signal intensity of carbonaceous deposits was further correlated with the data measured by TGA.

3. Results and discussion

3.1. Combined single-pass conversion of methane over SLC-6Mo/HMCM-49

The result of the combined single-pass conversion of methane on the SLC-6Mo/HMCM-49 catalyst system is shown in Figure 1. For comparison, the catalytic performances of the MDA reaction over the 6Mo/HMCM-49 catalysts with and without CO_2 in the CH_4 feed are also shown in figure 1. The advantage of the combined single-pass conversion is obvious. After running the combined reaction for 5 h on the SLC-6Mo/HMCM-49 catalyst systems, the CH_4 conversion and the yield of aromatics reached 15.4% and 8.9%, respectively, dropping to 10.9% and 6.0%, respectively, after 62 h on-stream. However, the deactivation of the 6Mo/HMCM-49 catalyst when used alone is pronounced. Though the aromatics yield was 10.7% at a methane conversion of 13.8% after 5 h on stream, it declined to 0.7% at a methane conversion of 2.7% after 38 h on stream. Only a small amount of CO yield could be found over the 6Mo/HMCM-49 catalyst, while it was in the range of 1.3–1.5% in the combined conversion of methane over the SLC-6Mo/HMCM-49 catalyst systems. Consistent with the higher yield of aromatics and longer lifetime, the coke selectivity in the early 20 h was also higher on the SLC-6Mo/HMCM-49 catalyst systems, as compared with that on the 6Mo/HMCM-49 catalyst. However, after running the reaction more than 20 h, the coke selectivity increases much more slowly with the SLC-6Mo/HMCM-49 catalyst compared with 6Mo/HMCM-49 alone. Moreover, the formation rate of hydrogen was kept to 1470 nmol s^{-1} $gcat^{-1}$ over the combined single pass mode after 80 h on stream, while it was dropped to 429 nmol s^{-1} $gcat^{-1}$ over the 6Mo/

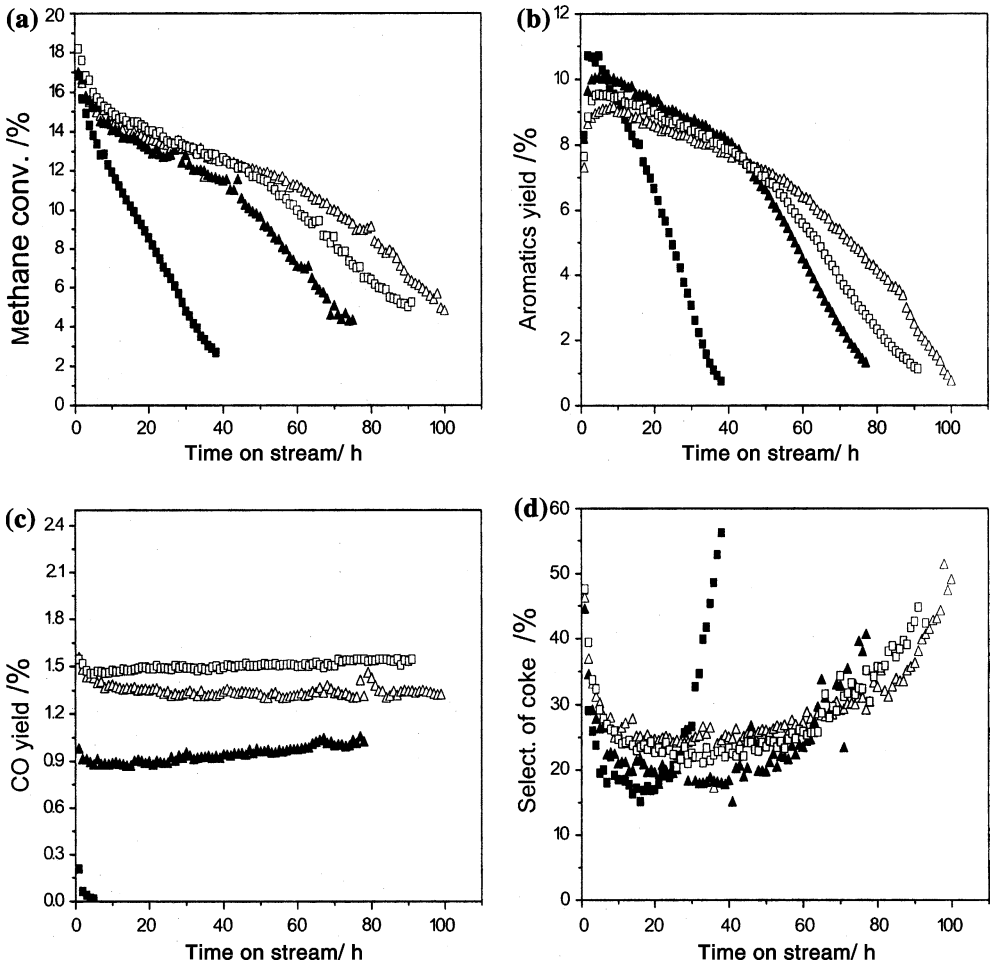

Figure 1. Change of methane conversion (a); aromatics yields (b); CO yields (c) and the selectivity to coke (d) with time on stream on 6Mo/HMCM-49, (■); SLC + 6Mo/HMCM-49, (△); 6Mo/HMCM-49 with 0.3% CO_2 in the CH_4 feed, (▲) and 6Mo/HMCM-49 with 0.6% CO_2 in the CH_4 feed (□).

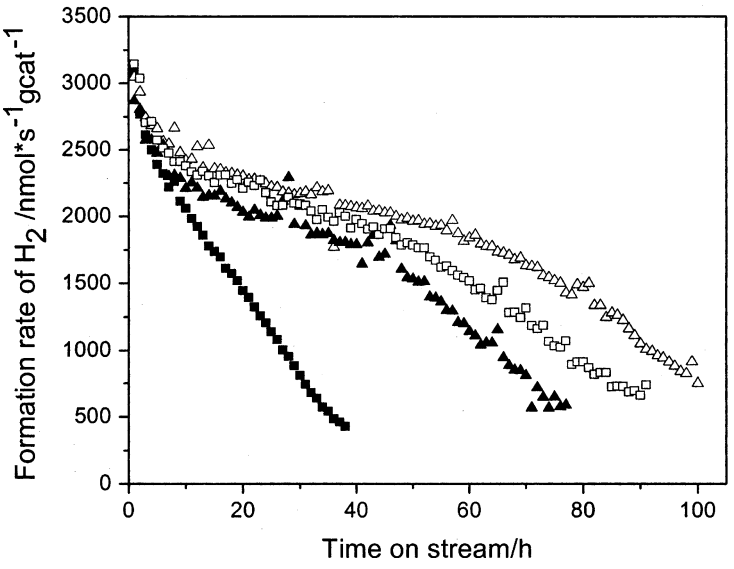

Figure 2. Changes of formation rate of H_2 with time on stream on different catalysts or under different reaction conditions. On 6Mo/HMCM-49, (■); SLC + 6Mo/HMCM-49, (△); 6Mo/HMCM-49 with 0.3% CO_2 in the CH_4 feed, (▲) and 6Mo/HMCM-49 with 0.6% CO_2 in the CH_4 feed, (□).

HMCM-49 catalyst after 38 h on stream, as shown in figure 2.

3.2. *Effect of CO_2 and H_2O on the combined conversion of CH_4 over the SLC-6Mo/HMCM-49 catalyst systems*

The catalytic performance of the OCM reaction over the SLC catalysts was evaluated first, the yield of C_2 species was about 1.3% with a C_2H_6/C_2H_4 ratio of 3.6 and under the selected reaction conditions. The yield of CO_2 was about 0.3% at a methane conversion of 1.6%, and no CO could be detected in the tail gas.

Ichikawa and coworkers have reported that the addition of CO_2 (less than 3%) to the CH_4 feed could enhance the Mo/HZSM-5 stability [14–17]. For comparison, the catalytic performance of MDA reaction over the 6Mo/HMCM-49 catalysts with CO_2 in the CH_4 feed also is shown in figure 1. The concentrations of CO_2 in the CH_4 feed were set to 0.3 and 0.6%, respectively.

With 0.3% CO_2 in the CH_4 feed, the CH_4 conversion was 15.2% and the yield of aromatics was 9.5% over the 6Mo/HMCM-49 catalyst after 5 h on stream. After running the reaction for 62 h, the CH_4 conversion and the yield of aromatics decreased to 6.9% and 3.5%, respectively. If the CO_2 level was doubled in the CH_4 feed, the 6Mo/HMCM-49 catalyst was not as stable as it was in the combined SLC-6Mo/HMCM-49 catalyst systems, as shown in figure 1. The CO yield increases with the increasing concentration of CO_2 in the CH_4 feed over the 6Mo/HMCM-49 catalyst. This confirms that the addition of CO_2 in the feed is an effective way to remove the coke via the reverse Boudouard reaction, i.e. $CO_2 + C = 2CO$. However, it appears that the addition of CO_2 in the feed is not the sole factor for improving the stability of the SLC-6Mo/HMCM-49 catalyst systems.

H_2O is another component in the tail gas of the OCM reaction (no CO was detected). It was estimated that about 56% of the oxygen was converted to H_2O, and the content of H_2O was 0.7% in the tail gas of the OCM over the SLC. Recently, the promotional effect of water for the MDA on Mo/HZSM-5 catalyst has been reported [18]. The authors claimed that the addition of 1.7% H_2O to the CH_4 feed displayed the best stability of the system at 998 K. A reasonable explanation is that the gasification of coke, i.e. $H_2O + C = CO + H_2$, would also play a role in eliminating the carbonaceous deposits. This was confirmed by further analyzing the H_2 formation rate from the combined single-pass reaction, as shown in figure 2. The main contribution to hydrogen formation is, of course, from the MDA reaction ($6CH_4 = C_6H_6 + 9H_2$). The addition of CO_2 into the CH_4 feed stabilized the 6Mo/HMCM-49 catalyst via the reverse Boudouard reactions on the coke species. As a result, the catalyst activity and the formation rate of H_2 are more stable, as shown in figure 2. The formation rate of H_2 in the combined conversion of methane over the SLC-6Mo/HMCM-49 catalysts was higher than that in the MDA reaction over the 6Mo/HMCM-49 catalyst when 0.3% or even 0.6% CO_2 was added in the CH_4 feed. Figures 1 and 2 show the combined effect of CO_2 and H_2O yielded by the OCM reaction improves the combined single-pass conversion of methane over the SLC-6Mo/HMCM-49 catalyst system and is a more effective way to prolong the life of MDR catalyst than by the addition of CO_2 alone.

The deactivation rate constants, k_d, of the different reaction feeds (with or without CO_2 in the CH_4 feed) on

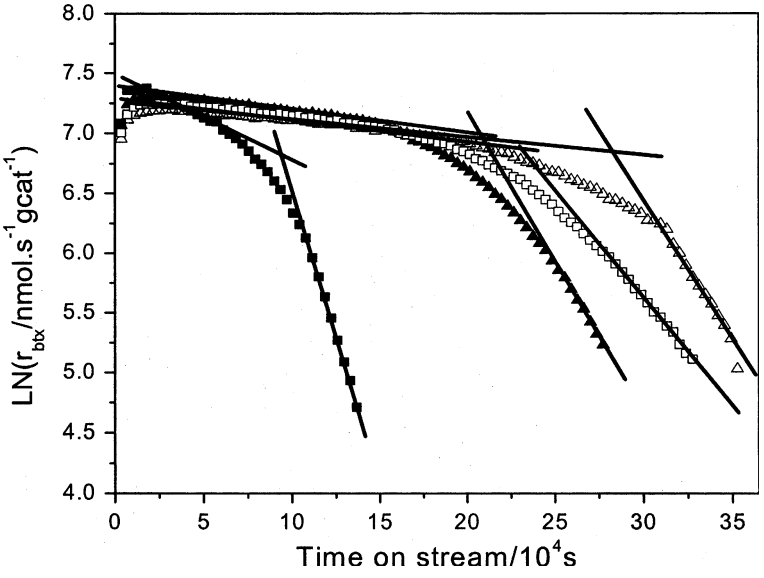

Figure 3. Deactivation curves on different catalysts or under different reaction conditions. On 6Mo/HMCM-49, (■); SLC + 6Mo/HMCM49, (△); 6Mo/HMCM-49 with 0.3% CO_2 in the CH_4 feed, (▲) and 6Mo/HMCM-49 with 0.6% CO_2 in the CH_4 feed, (□).

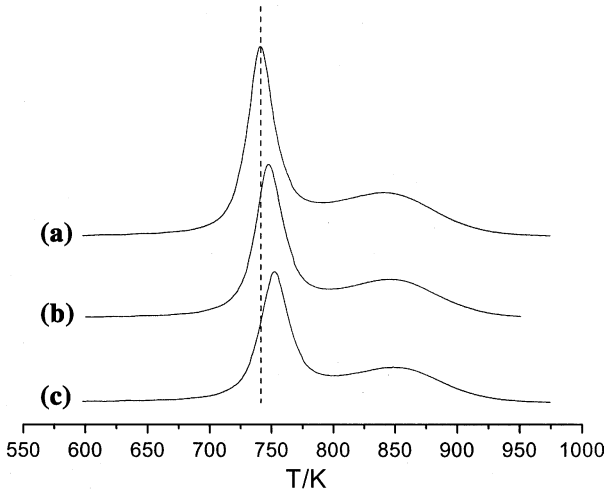

Figure 4. Typical TPO profiles of the coked catalysts after running the reaction for 5 h. (a) 6Mo/HMCM-49, (b) 6Mo/HMCM-49 with 0.3% CO_2 in the CH_4 feed, and (c) SLC + 6Mo/HMCM-49.

various catalysts, were calculated from the deactivation curves by plotting the natural logarithm of the BTX formation rate versus the reaction time on stream according to ref. [27], and shown in figure 3. The deactivation curves can be divided into three regions. The first one is a progressive deactivation region in which the catalyst deactivated smoothly, and the third one is a rapid deactivation region, shown in figure 3. The second one is a transition deactivation region between the progressive and rapid deactivation regions. As far as the first deactivation range is concerned, the k_{d1} is 7.2×10^{-6} s^{-1} for the MDA reaction over the Mo/MCM-49 catalysts, reducing to 1.9×10^{-6} s^{-1} with addition of CO_2 into the CH_4 feed, while it is 1.5×10^{-6} s^{-1} for the combined conversion of methane over the SLC-6Mo/HMCM-49 catalyst system. The results implied that the combined reaction of CH_4 on the SLC-6Mo/HMCM-49 catalyst system is a more efficient approach to stabilize the MDA reaction than addition of CO_2 into the CH_4 feed.

3.3. TPO and TG analysis over the used catalysts

Figure 4 shows typical TPO profiles from the used 6Mo/HMCM-49 catalysts under different reaction condition. All the TPO profiles consist of a sharp peak of low temperature and a broad one of high temperature. A similar double-peak feature from coked Mo based zeolite catalysts has been reported in the literature [16,27,28]. Ichikawa and his coworkers attributed the low-temperature peak (<673 K) to a reactive coke associated with Mo_2C and the high-temperature one to irreversible or inert coke [16]. Both types can be suppressed by the addition of a small amount of CO, CO_2 or H_2O, which also result in improved stability compared with using pure CH_4 as the feed gas [14–18]. The results of TG and TPO from the used catalysts after running for different durations are shown in Table 1. As expected, the amount of coke thus estimated is in the following sequence: the least on the 6Mo/HMCM-49 taken from the combined conversion of CH_4 over the SLC-6Mo/HMCM-49 catalyst systems, and the highest on the 6Mo/HMCM-49 without CO_2 in the CH_4 feed. Table 1 also revealed that coke that was burnt-off at low temperatures increased much more quickly than coke burnt-off at high temperatures with increased in the reaction time.

4. Conclusions

The combined single-pass conversion of methane via oxidative coupling and dehydroaromatization over the SLC-6Mo/HMCM-49 catalyst system shows a more effective improvement in the performance of methane dehydro-aromatization, which could be attributed to an efficient removal of the carbon deposition on 6Mo/HMCM-49 catalyst via the CO_2 and H_2O generated in OCM process.

Table 1
TG and TPO results obtained from the used catalysts after running the reaction for different durations of time

Catalyst	6Mo/HMCM-49		6Mo/HMCM-49 with 0.3% CO_2 in CH_4 feed		SLC + 6Mo/HMCM-49	
Time on stream, h	Peak Temp., K	Coke amounts, mg/gcat	Peak Temp., K	Coke amounts, mg/gcat	Peak Temp., K	Coke amounts, mg/gcat
5	743	49	749	43	752	39
	837	38	843	31	844	32
		87[a]		74		71
21	782	102	786	101	791	90
	859	50	861	45	863	39
		152		146		129
62	838	223	808	200	813	166
	900	97	882	54	882	48
		320		254		214

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