Combined single-pass conversion of methane via oxidative coupling and dehydroaromatization

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A new reaction mode, i.e., the combined single-pass conversion of methane via oxidative coupling (OCM) over mixed metal oxide (SLC) catalysts and dehydroaromatization (MDA) over Mo/HZSM-5 catalysts, is reported. With the assistance of an OCM reaction over SLC catalysts in the top layer of the reactor, the deactivation resistance of Mo/HZSM-5 catalysts is remarkably enhanced. Under the selected reaction conditions, the CH_4 conversion decreased from ~18 to ~1% and the aromatics yield decreased from 12.8 to 0.1%, respectively, after running the reaction for 960 min on both 6Mo/HZSM-5 and SLC-6Mo/HZSM-5 catalyst system without O_2 in the feed. On the other hand, for the SLC-6Mo/HZSM-5 catalyst system with O_2 in the feed, the deactivation was improved greatly, and after 960 min onstream the CH_4 conversion and aromatics yield were still as high as 12.0 and 8.0%, respectively. The promotion effect mainly appears to be associated with *in situ* formation of CO_2 in the OCM layer, which reacts with coke via the reverse Boudouard reaction.

KEY WORDS: single-pass; methane; oxidative coupling; dehydroaromatization; aromatics.

1. Introduction

Direct conversion of methane into valuable chemicals is one of the great challenges faced by catalytic chemists. Two approaches involve the direct conversion of methane with the assistance of oxidants and the direct conversion of methane under nonoxidative conditions. The former is thermodynamically more favorable than the latter. However, the selective oxidation of methane into methanol and the oxidative coupling of methane (OCM) are both limited by the yield of the desirable product due to secondary reactions and the coproduction of CO_x [1,2]. Since 1993, methane dehydroaromatisation (MDA) over Mo/HZSM-5 catalysts under nonoxidative conditions has received great attention since the catalytic results were close to those predicted by thermodynamics at ca. 973 K [3–6]. Until now, the Mo-modified HZSM-5 catalyst is the most active one among the tested catalysts. However, heavy formation of carbonaceous deposits is one of the most serious obstacles in making the reaction of practical interest.

To improve the activity and stability of the Mo/HZSM-5 catalyst, many approaches, such as modification of the chemical compositions of the transition metal ions and adjustment of the acidity of the HZSM-5 zeolite or the usage of the other zeolites, have been studied [4–6]. Addition of co-reactants to the CH_4 feed is also an effective way to inhibit deactivation and to influence the reaction rates and selectivities. For example, the addition of a small amount of CO_2 (less than 3%) to the CH_4 feed enhanced the catalyst stability [7–10]. Recently, Eglesia and coworkers [11] have studied the effects of CO_2, CO, and H_2 co-reactants on methane reactions catalyzed by Mo/H-ZSM-5. The authors concluded that CO_2 co-reactants increased catalyst stability and decreased the molecular weight of the products during the MDA reaction by the scavenging of CH_x species formed in the CH_4 activation steps. However, the total CH_4 conversion rates were not affected by CO_2 addition. Hydrogen formed near the bed inlet during CH_4 activation is responsible for the lower deactivation and pyrolysis rates in the rest of the catalyst bed. Mo_2C/HZSM-5 catalysts were also reported to be effective catalysts in the conversion of C_2H_6 into C_6H_6 at 773–973 K [12]. At 973 K, the conversion of C_2H_6 was ca. 67% and the selectivity to C_6H_6 was ca. 31%.

Researchers have also examined methane transformation into aromatics in the presence of O_2. For example, a trace of O_2 in the feed could remove some of the coke deposits on Mo/HZSM-5 and thereby enhance its activity and stability [13]. Liu *et al.* tested the catalytic transformation of CH_4 into styrene in the presence of O_2 over a well-mixed catalyst of $La_2O_3 + MoO_3$/HZSM-5 [14]. Styrene selectivity of 10.8% at a methane conversion of 18.3% was obtained with a CH_4/O_2 (6/1 mole ratio) mixture at 1023 K. Because the concentration of O_2 in the feed was high, it is unclear whether the Mo species involved were in the carbide and/or oxycarbide state, which are recognized as the active species for the methane activation

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and dehydrogenation under nonoxidative conditions [15–20].

In order to save raw materials and energy, chemists around the world have been trying to facilitate chemistry as nature performs in the cells of organisms, i.e., by going through a multistep catalytic reaction to convert starting material to the final product without separation of intermediates [21]. The mutual compatibility and high selectivity of the enzymatic conversions make it possible to proceed without the intermediate recovery steps. A so-called "one pot" synthesis, proceeding without separation, is now highlighted in the fields of organic synthesis and homogeneous catalysis.

Inspired by the idea of the "one pot" reactions, we suspected that the OCM is, perhaps, a possible approach to produce a tail gas, which contains concurrently C_2, CO_x, and traces of O_2, all of which, as mentioned above, are beneficial to the MDA reaction for enhancing its activity and stability. Our early studies demonstrated that 20 wt% SrO–20 wt% La_2O_3/CaO (SLC) is a reasonably good catalyst for the OCM reaction [22,23]. In this work, we put the SLC catalysts in the top layer and the Mo/HZSM-5 catalysts in the second layer in a fixed-bed reactor, so that the OCM and MDA reactions could be explored in combination to give improved single-pass conversions.

2. Experimental

The Mo/HZSM-5 catalyst was prepared by the conventional impregnation method as previously described [24,25]. HZSM-5 zeolite with a $SiO_2/Al_2O_3 = 50$ was supplied by Nankai University (Tianjin, China). It 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 4 h. In this work, the Mo content of the Mo/HZSM-5 catalysts was 6 wt% and, hereafter, they are denoted as 6Mo/HZSM-5. In one case, the 6Mo/HZSM-5 catalysts were treated by steam for 30 min and denoted as 6Mo/HZSM-5(I) [26]. In another case, HZSM-5 was first treated by an alkali solution in order to create mesopores and was denoted as 6Mo/HZSM-5(II) [27]. For brevity, in some cases, HZSM-5 is abbreviated as HZ.

The 20 wt% SrO–20 wt% La_2O_3/CaO (SLC) catalysts were prepared by the coprecipitation method. An $(NH_4)_2CO_3$ 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 pressed, crushed and sorted into sizes of 20–40 meshes and stored in a desiccator before use.

The catalytic tests were carried out in a quartz tubular fixed-bed reactor at atmospheric pressure and a temperature of about 983 K. The charge of the SLC catalyst was 0.1 g and that of the 6Mo/HZSM-5 catalysts was 1.0 g. The SLC catalyst was set as the top layer and the 6Mo/HZSM-5 catalysts were set as the second layer within the reactor. The catalysts were first heated under an He stream to the reaction temperature and maintained at this temperature for 30 min. After the pretreatment, the reactant gas was introduced into the reactor at a space velocity of 1500 mL/g/h. The tail gas was regularly and automatically sampled and analyzed by a Varian 3800 on-line gas chromatograph, which was equipped with a flame ionization detector (FID) for the analysis of CH_4, C_6H_6, C_7H_8, $C_{10}H_{12}$ and a thermal conductivity detector (TCD) for the analysis of H_2, N_2, CH_4, CO, C_2H_4, and 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 Lunsford and coworkers [18]. The reaction results were expressed as methane conversions; and the yields, the formation rates and the selectivities toward the products such as C_6H_6, C_7H_8, and $C_{10}H_8$, etc., were calculated on the basis of the converted methane molecules, as described in [28].

3. Results and discussion

3.1. Fine-tuning the reaction condition of combined single-pass conversion of methane over SLC and 6Mo/HZSM-5 catalysts systems at 983 and 1023 K

In our initial studies on combined single-pass conversion of CH_4 via oxidative coupling and dehydroaromatization, we found that the reaction conditions such as reaction temperature, feed composition (the ratio of $CH_4 : O_2$) and corresponding loadings of SLC and Mo/HZSM-5 are critical in allowing the desired OCM and MDA reactions to proceed effectively. The catalyst charge was set at 0.1 g for the OCM catalyst and at 1.0 g for the MDA. The concentration of O_2 was found to be a key factor since too much O_2 left behind from the OCM catalyst layer is harmful, as it maintains molybdenum in an oxidized form, which is inactive for the MDA. Producing more C_2 as well as a suitable amount of CO_2 in the OCM is desirable for the subsequent MDA reaction. Extremely high CH_4/O_2 ratios in the range of 9:0.24 to 9:0.06 (in volume) at 1003 K were tested over SLC-6Mo/HZSM-5 catalyst system and the selected results are listed in table 1 and shown in figures 1 and 2. In the early stage of the reaction, i.e., with the time on-stream of 60 min, the methane conversion and the selectivities of coke and CO increased, while the selectivity to different aromatics decreased with increasing concentration of oxygen in the feed (see table 1). However, the best stability and the yields of aromatics for the combined catalyst system were obtained at the CH_4/O_2 ratio of 9:0.12 and after running the reaction for 1410 min, the aromatics yield was 7.7% at a methane conversion of 12.8%.

Table 1
The combined single-pass conversion of methane via OCM and MDA over SLC-6Mo/HZSM-5 catalyst system under different reaction conditions

Temp. (K)	$CH_4:O_2:X$[a]	CH_4 Conv. (%)	Selectivity, %							Aromatics yield (%)[b]
			CO	C_2	C_6H_6	C_7H_8	C_8H_{10}	$C_{10}H_8$	Coke	
983	9:0.12:1.2[a]	17.1	16.5	1.7	42.7	2.4	0.2	11.2	25.3	9.7
983	9:0.12:1.2[b]	14.0	20.8	2.8	52.4	3.7	0.3	5.7	14.4	8.7
983	9:0.12:1.2[c]	13.3	21.1	3.1	51.7	3.8	0.4	4.7	15.2	8.1
1003	9:0.06:1.1[a]	17.7	8.3	1.9	50.3	2.9	0.2	13.3	24.0	11.6
1003	9:0.06:1.1[b]	12.5	12.4	5.0	67.9	5.3	0.6	4.9	4.0	9.8
1003	9:0.06:1.1[c]	7.2	20.4	13.4	44.4	2.4	0.3	2.5	16.6	3.6
1003	9:0.12:1.2[a]	19.3	14.2	1.8	47.0	2.6	0.2	10.1	24.1	11.6
1003	9:0.12:1.2[b]	14.3	19.4	3.6	54.0	4.2	0.5	4.0	14.5	9.0
1003	9:0.12:1.2[c]	12.8	22.6	4.6	52.1	3.9	0.4	3.3	13.1	7.7
1003	9:0.24:1.3[a]	20.7	23.7	1.5	32.6	1.8	0.1	7.0	33.3	8.6
1003	9:0.24:1.3[b]	16.4	30.0	2.7	30.7	2.1	0.2	2.7	31.5	5.9
1003	9:0.24:1.3[c]	15.3	32.0	3.1	29.1	2.2	0.2	2.1	31.2	5.2
1023	9:0.12:1.2[a]	17.7	16.6	2.3	47.1	3.1	0.4	5.6	24.9	9.9
1023	9:0.12:1.2[d]	10.3	28.1	9.3	38.7	3.6	0.9	1.7	17.7	4.6

[a] X included He and N_2.
[b] Aromatics yields include C_6H_6, C_7H_8, C_8H_{10}, and $C_{10}H_8$.
Note: Data were taken after running the reaction for [a]60 min; [b]960 min; [c]1410 min; [d]480 min.

A ratio of CH_4 to O_2 of about 9:0.12 (in volume) was selected, and the temperature was varied from 983 to 1023 K. Selected results are also listed in table 1. The reaction temperature of 1023 K was too high to allow the combined conversion to proceed effectively. The initial catalytic results at 60 min at 1023 K were similar to those at 983 K, but the catalyst system deactivated very fast, and after running the reaction for 480 min, the aromatics yield decreased from 9.9 to 4.6%.

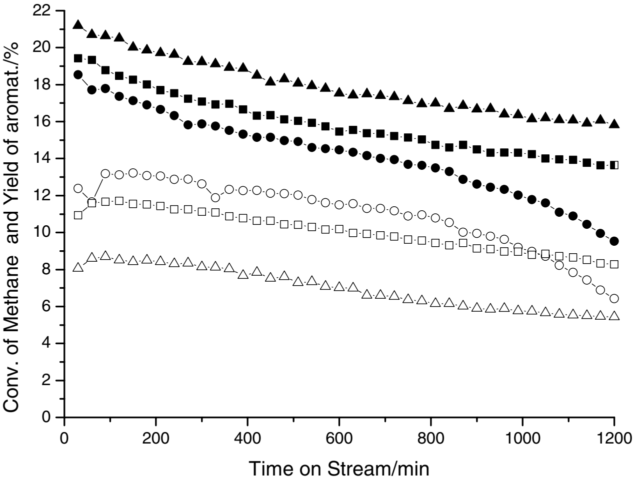

Figure 1. Changes of the methane conversion (solid symbols) and aromatics yields (empty symbols) over SLC-6Mo/HZSM-5 catalyst system with different ratios of CH_4 to O_2 at 1003 K with time on-stream. $CH_4:O_2:X = 9:0.24:1.3$ (▲, △); $CH_4:O_2:X = 9:0.12:1.2$ (■, □); and $CH_4:O_2:X = 9:0.06:1.1$ (●, ○).

Catalytic behavior of 6Mo/HZSM-5 and SLC-6Mo/HZSM-5 catalyst system without O_2 addition in the feed after running the reaction for 60 and 960 min at 1003 K is listed in table 2. The OCM result on the SLC is included in table 2 for reference. The selectivities to C_2 and CO_2 are about 90 and 10% at the methane conversion of 4%. No obvious difference in catalytic performance could be observed on the 6Mo/HZSM-5 and the SLC-6Mo/HZSM-5 catalyst system if oxygen was not added in the feed.

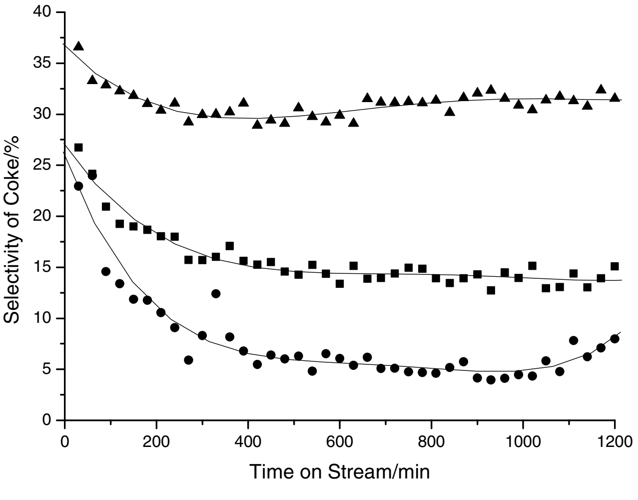

Figure 2. Changes of the selectivity to coke over SLC-6Mo/HZSM-5 catalyst system with different ratios of CH_4 to O_2 at 1003 K with time on-stream. $CH_4:O_2:X = 9:0.24:1.3$ (▲); $CH_4:O_2:X = 9:0.12:1.2$ (■); and $CH_4:O_2:X = 9:0.06:1.1$ (●).

Table 2
The combined single-pass conversion of methane via OCM and MDA on different catalyst systems at 1003 K

Catal.	CH_4 Conv. (%)	Selectivtiy, %							Aromatics Yield/ H_2 conc. (%)[a]
		CO/CO_2	C_2	C_6H_6	C_7H_8	C_8H_{10}	$C_{10}H_8$	Coke	
6Mo/HZ[a,d]	17.9	0	2.3	55.3	3.4	0.3	11.8	27.0	12.7/17.1
6Mo/HZ[b,d]	0.9	0	25.0	7.2	0.8	0.0	0.0	67.0	0.1/1.1
SLC-6Mo/HZ[a,d]	18.7	0	2.1	53.9	3.2	0.3	12.5	28.1	13.0/17.7
SLC-6Mo/HZ[b,d]	0.9	0	17.9	8.2	0.6	0.5	0.2	72.5	0.1/1.1
SLC-quartz[a,e]	3.9	0/9.3	90.7	–	–	–	–	–	–
SLC-6Mo/HZ[a,e]	17.7	12.8/0	2.3	56.3	3.3	0.3	9.3	15.7	12.3/19.2
SLC-6Mo/HZ[b,e]	12.0	21.7/0	5.1	57.7	4.5	0.7	3.6	6.7	8.0/13.6
SLC-6Mo/HZ(I)[a,e]	18.4	14.2	1.8	54.5	3.1	0.2	10.1	16.2	12.5/19.9
SLC-6Mo/HZ(I)[b,e]	15.3	18.2	3.0	64.1	4.5	0.5	4.5	5.2	11.3/16.7
SLC-6Mo/HZ(I)[c,e]	13.0	19.2	4.4	59.7	4.0	0.5	4.0	8.1	8.8/14.3
SLC-6Mo/HZ(II)[a,e]	18.5	13.7	1.7	50.3	2.8	0.2	12.0	19.2	12.1/19.7
SLC-6Mo/HZ(II)[b,e]	14.4	17.6	3.4	61.7	4.4	0.5	5.0	7.4	10.3/15.8
SLC-6Mo/HZ(II)[c,e]	10.7	24.4	6.8	52.1	3.3	0.4	3.6	9.5	6.4/10.0

[a]Aromatics yields include C_6H_6, C_7H_8,C_8H_{10}, and $C_{10}H_8$ and H_2 concentration in tail gas was calculated on the basis of on-line GC analysis. *Note*: Data were taken after running the reaction for [a]60 min, [b]960 min, [c]1680 min. The feed composition was [d]$CH_4:N_2 = 9:1$ and [e]$CH_4:O_2:N_2 = 9:0.11:1$. N_2 was used as an internal standard and the loading of SLC was 0.1 g and that of 6Mo/HZ was 1.0 g.

When O_2 was added into the feed with a ratio of CH_4 to O_2 of about 9:0.11, the OCM reaction on the SLC catalysts started working, and the catalytic results on the SLC-6Mo/HZSM-5 catalyst system were unique. In the early stage of the reaction (at 60 min), the CH_4 conversion and the selectivity to hydrocarbons on the SLC-6Mo/HZSM-5 catalysts with O_2 in the feed were almost the same as those on the 6Mo/HZSM-5 catalyst without O_2 in the feed, but the selectivity to CO increased from 0 to 12.8% and the selectivity to coke deposits decreased from 28.1 to 15.7% as we can see from table 2. Simultaneously, the hydrogen concentration in the tail gas increased from 17.7 to 19.2%.

The deactivation of the 6Mo/HZSM-5 and SLC-6Mo/HZSM-5 catalyst system was very serious when there was no O_2 in the feed. The CH_4 conversion decreased from about 18 to 1% and the aromatics yield decreased from 12.8 to 0.1%, respectively, after running the reaction for 960 min. On the other hand, for the SLC-6Mo/HZSM-5 catalyst system with O_2 in the feed, the deactivation was improved greatly, and after 960 min on-stream the CH_4 conversion and aromatics yield were still as high as 12.0 and 8.0%, respectively.

It is interesting to note that the selectivity toward the coke changed with time on-stream on the 6Mo/HZSM-5 without O_2 in the feed and the SLC-6Mo/HZSM-5 catalyst system with O_2 in the feed. On the catalyst systems with combined conversion, the selectivity to coke decreased with the time on-stream from 15.7 to 6.7%. However, it increased from 27 to 67% on the 6Mo/HZSM-5 catalysts. On the other hand, the selectivity to CO increased on the SLC-6Mo/HZSM-5 catalyst system. Since only CO_2 could be detected in the tail gas on the SLC catalyst, and only CO could be detected in the tail gas on the SLC-6Mo/HZSM-5 catalyst system with O_2 in the feed, the reverse Boudouard reaction occurred between CO_2 molecules formed in the OCM and the coke formed in the MDA, thus removing the coke or inhibiting its formation on the 6Mo/HZSM-5 catalysts. Additionally, a small amount of water could be detected in the OCM reaction and the H_2 concentration in the tail gas increased from 17.7 to 19.2% as compared to the results obtained on the SLC-6Mo/HZSM-5 catalyst system with O_2 in the feed to that without O_2 in the feed on the same catalyst system; the gasification of coke by water may also make a small part of the contribution.

3.2. *Combined single-pass conversion of methane over SLC and modified 6Mo/HZSM-5 catalyst systems*

In our studies of the MDA reaction, we have found that dealumination of the Mo/HZSM-5 catalysts by steam treatment [26], as well as a proper alkali treatment to the HZSM-5 zeolite for creating mesopores, which can improve mass transport [27], are both effective procedures for enhancing the activity and stability of the Mo/HZSM-5 catalyst. Therefore, the combined single-pass conversion of methane via oxidative coupling and dehydroaromatization was further tested and evaluated with the SLC-6Mo/HZSM-5(I) and the SLC-6Mo/HZSM-5(II). Catalytic reaction results for these two catalyst systems are also listed in table 2 and are shown in figure 3. Indeed, the yield of the aromatics in the early stage of the reaction (after running the reaction for

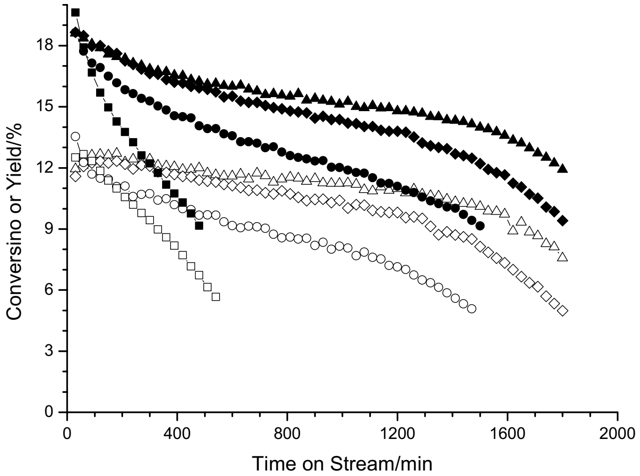

Figure 3. Changes of the methane conversion (solid symbols) and aromatics yields (empty symbols) on different catalyst systems with time on-stream. On 6Mo/HZ (■ □); on SLC-6Mo/HZ (●, ○); on SLC-6Mo/HZ(I) (▲, △); on SLC-6Mo/HZ(II) (◆, ◇). 6Mo/HZ(I) denotes the catalyst pretreated by steam for 0.5 h and HZ(II) denotes the zeolite pretreated by an alkali solution.

60 min) did not change very much in all cases, and amounted to ca. 12%. However, deactivation of the catalyst is suppressed, particularly in the case of the SLC-6Mo/HZSM-5(I) catalyst system. After running the reaction for 1680 min, the yield of aromatics was ca. 8.8% at a CH_4 conversion of 13.0%. With more active and stable MDA catalysts, higher activity and stability was also achieved using combined single-pass conversion of methane via oxidative coupling and dehydroaromatization.

It is interesting to note that at 1003 K with a ratio of CH_4 to O_2 of about 9:0.12 (in volume), there was an increase in the deactivation on all the combined catalyst systems when running the reaction for more than about 1200 min. We suspect that one possible reason is the loss of Mo species under such a high reaction temperature and the other one is the accumulation of coke deposits, which at last block the pore channels. The study on this point is now underway in our laboratory.

4. Conclusions

The present work shows that the combined single-pass conversion of methane via oxidative coupling and dehydroaromatization over the SLC-6Mo/HZSM-5 catalyst system is an effective way for enhancing the activity and stability of the 6Mo/HZSM-5 catalysts. This enhancement appears to be due to the formation of CO_2 in the OCM reaction over SLC catalysts, which reacts via the reverse Boudouard reaction with coke formed in the MDA reaction on 6Mo/HZSM-5 catalysts.

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