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Methane aromatization over 2 wt% Mo/HZSM-5 in the presence of O_2 and NO

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In the non-oxidative aromatization reaction (temperature = 770 °C, flow rate = 34 ml min^{-1}), 2 wt% Mo/HZSM-5 deactivated after 4 h due to severe coking. We observed that with a suitable amount of O_2 ($\leq$5.3 vol%) in the methane feed, the catalyst could last for more than 6 h with a *ca.* 4% yield of aromatics at 770 °C. Depending on the concentration of O_2 or the reaction temperature, there are three reaction zones in the catalyst bed: (i) methane oxidation; (ii) methane reforming; and (iii) methane aromatization. CO and H_2 produced in the first two zones are accountable for stability amelioration of the catalyst. The addition of NO exhibited similar effects on the reaction. Further increase in O_2 ($\geq$8.4 vol%) or NO ($\geq$14.2 vol%) concentration would result in CO and CO_2 being the predominant carbon-containing products; C_2H_4 and C_2H_6 were generated in small amounts and no aromatics were detected.

KEY WORDS: methane aromatization; Mo/HZSM-5; oxygen and nitric oxide addition

1. Introduction

The conversion of methane to value-added aromatic compounds bears significant economic implications [1]. In view of the facts that the reaction is equilibrium limited and catalyst deactivation caused by severe coking is common, the feasibility of methane dehydroaromatization in the presence of an oxidant, especially oxygen, is of particular interest.

By using a mixture of methane and oxygen ($CH_4 : O_2 : N_2 = 10:1:4$), Claridge *et al.* [1] obtained 13.2% methane conversion and 23.4% aromatics selectivity (yield = 3.1%) over NaCl/MnO_2 at 950 °C and at an elevated pressure of 6 atm. Earlier, Otsuka *et al.* [2] synthesized aromatic hydrocarbons by passing methane and oxygen through a system of two catalyst beds, *i.e.*, NaCl/Mn-oxide active for the oxidative coupling reaction of methane (OCM) and Ga/HZSM-5 (Si/Al = 25) active for converting C_{2+} hydrocarbons to aromatics; by so doing, they obtained an aromatics yield of 5.6%. Lin *et al.* [3] reported a methane conversion of 18.3% and a styrene selectivity of 10.8% (yield = 2.0%) over a mixed catalyst La_2O_3 + Mo/HZSM-5; the reaction conditions adopted were $CH_4 + O_2$ (6:1 mole ratio) at 750 °C and 3500 ml h^{-1}. In these cases, ethylene, ethane or methyl radical ($CH_x^{\bullet}$) produced over the basic catalysts *via* OCM reactions were considered to be further oligomerized and cyclized to aromatic compounds.

In 1983, the production of higher hydrocarbons (C_{5+}) directly from methane and oxygen over HZSM-5 was first reported by Shepelev and Ione [4] but the results were unreproducible [5–7]. Han and co-workers [8,9] reported that HZSM-5 zeolite had little influence on product selectivity; methanol was the only non-CO_x product. However, some transition-metal-containing ZSM-5 catalysts, such as Zn(Cu or Ni)/HZSM-5, have been reported to be effective for the production of C_{5+} liquids from methane and oxygen if dehydrogenation and oxidation functions of the metal are in balance [9].

Recently, extensive studies have been conducted over 2–3% Mo/HZSM-5 for the non-oxidative dehydroaromatization of methane [10–17]; despite severe coking, the catalysts performed reasonably well. Ohnishi *et al.* [18] have reported that a few percent of co-fed oxygen would inhibit completely the formation of benzene over Mo/HZSM-5 at 700 °C. The results of Lin *et al.* indicated very low selectivity toward aromatic compounds; a yield of only *ca.* 0.2% at 750 °C and 3500 ml h^{-1} was reported [3]. Yuan *et al.* [19], however, reported that a small extent of oxygen addition might result in a partial removal of coke deposit on Mo/HZSM-5, and with the catalyst being kept as MoO_xC_y/HZSM-5, there was an improvement in catalytic performance. The critical concentrations of oxygen for oxidative aromatization were *ca.* 0.7, 3, and 7 vol% at 700, 750 and 800 °C, respectively. Our present work is to investigate further the effect of oxygen addition on methane dehydrogenation and aromatization over 2 wt% Mo/HZSM-5.

2. Experimental

2.1. Catalyst preparation

The 2 wt% Mo/HZSM-5 catalyst was prepared by impregnating HZSM-5 (Si/Al = 25, Nankai University,

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P.R. China) with a desired amount of ammonium heptamolybdate in aqueous solution at room temperature for 24 h. The catalyst was then dried at 120 °C for 6 h and calcined in air at 500 °C for 5 h. The calcined samples were crushed and sieved to 20–40 mesh for catalytic evaluation.

2.2. Catalytic evaluation

Catalytic reactions were carried out at atmospheric pressure in a continuous fixed-bed quartz microreactor (i.d. 8 mm) packed with 1 g of catalyst. After the catalyst was pretreated in a flow of He (25 ml min^{-1}) at 700 °C for 30 min, pure methane or a feed gas mixture of $CH_4 + O_2$ (or NO) was introduced into the reactor at a flow rate of 34 ml min^{-1} through a Brooks mass flow controller. The outlet pipeline and the sampling valve were kept slightly higher than 160 °C. The reaction mixtures were analyzed on-line by gas chromatography using a column containing 5% Bentone 34 on Chromosorb W-AW for the separation of aromatic products and a HayeSep D column for the separation of CH_4, CO, CO_2 and other light hydrocarbons. A 5A Molecular Sieve column was used for the separation of H_2, O_2 and N_2. Methane conversion and product selectivity were calculated on a carbon number basis.

2.3. Catalyst characterization

The specific surface area and pore volume of the samples were measured by means of the BET method on a NOVA 1200 instrument. Nitrogen was used as the adsorbate. All of the samples were outgassed at 300 °C for 2 h before measurements.

The temperature-programmed desorption of NH_3 was performed to determine the acidity of the Mo/HZSM-5 samples. The sample (0.1 g) was first heated at 600 °C for 40 min and then cooled down to room temperature in He before being exposed to a NH_3/He mixture of 8 vol% ammonia for 30 min. After NH_3 exposure, the sample was He-purged for 1 h and then heated (10 °C min^{-1}) from room temperature to 600 °C. A thermal conductivity detector was employed to monitor the amount of ammonia in the effluent.

The X-ray photoelectron spectra were obtained by operating an ESCALAB MK-II spectrometer (Al Kα 1486.6 eV, 15 mA and 15 kV). The Si 2p line at 103.4 eV was taken as a reference for binding energy calibration.

3. Results and discussion

The catalytic performance of 2 wt% Mo/HZSM-5 as a function of reaction temperature (T_r) after 1 h of non-oxidative reaction at a reactant flow of 34 ml min^{-1} is summarized in table 1. One can observe that Mo/HZSM-5 gave 1.5% CH_4 conversion, 1.3% aromatics yield, and 0.2% C_2-hydrocarbon (C_2H_4/C_2H_6 ratio = 0.7 : 1) yield at $T_r = 600$ °C. With a rise in T_r from 600 to 770 °C, the methane conversion, C_2-hydrocarbon and aromatics yields as well as the C_2H_4/C_2H_6 ratio increased. At $T_r = 770$ °C, 9.3% methane conversion, 8.4% aromatics and 0.9% C_2-hydrocarbon yields were obtained; the C_2H_4/C_2H_6 ratio reached 4.6 : 1. Apparently, a rise in T_r from 650 to 770 °C was beneficial not only for methane activation but also for the oligomerization and cyclization of ethylene to aromatics.

Shown in figure 1 is the catalytic performance of 2 wt% Mo/HZSM-5 during 6 h of on-stream reaction at 34 ml min^{-1}. At $T_r = 600$ or 650 °C, both aromatics and C_2-hydrocarbon yields were stable; after 6 h at $T_r = 700$ °C, there was a decrease in aromatics yield from 5.9 to 2.5% but an increase in C_2-hydrocarbon yield from 0.5 to 1.1%. At $T_r = 770$ °C, the catalyst deactivated for aromatization after *ca.* 4 h; the C_2-hydrocarbon yield and the C_2H_4/C_2H_6 ratio first increased and then drastically decreased. The highest C_2-hydrocarbon yield was *ca.* 1.8% after 3 h.

Coke deposition is considered to be the main cause for the gradual deactivation of Mo/HZSM-5 in methane non-oxidative aromatization [18–20]. Figure 2 shows the NH_3–TPD results after ammonia adsorption at room temperature. For a fresh Mo/HZSM-5 sample, there were desorptions at 110, 225 and 456 °C. The one at 110 °C has been assigned to the desorption of physisorbed NH_3 whereas the one at 456 °C to NH_3 strongly

Table 1
Effects of reaction temperature (T_r) on methane aromatization in the absence of an oxidant[a]

T_r (°C)	CH_4 conversion (mol%)	Selectivity (mol%)					Yield (mol%)		$C_2H_4 : C_2H_6$
		C_2H_4	C_2H_6	C_6H_6	C_7H_8	$C_{10}H_8$	C_2	Aromatics	
600	1.5	6.8	10.2	83.0	—	—	0.2	1.3	0.7 : 1
650	2.8	5.4	4.9	81.8	2.3	5.6	0.3	2.5	1.1 : 1
700	6.4	5.2	2.1	77.9	2.1	12.7	0.5	5.9	2.5 : 1
770	9.3	7.8	1.7	70.2	1.9	18.4	0.9	8.4	4.6 : 1

[a] Data were recorded *ca.* 1 h after the start of the reaction; flow rate: 34 ml min^{-1}.
C_2: C_2H_4 and C_2H_6.

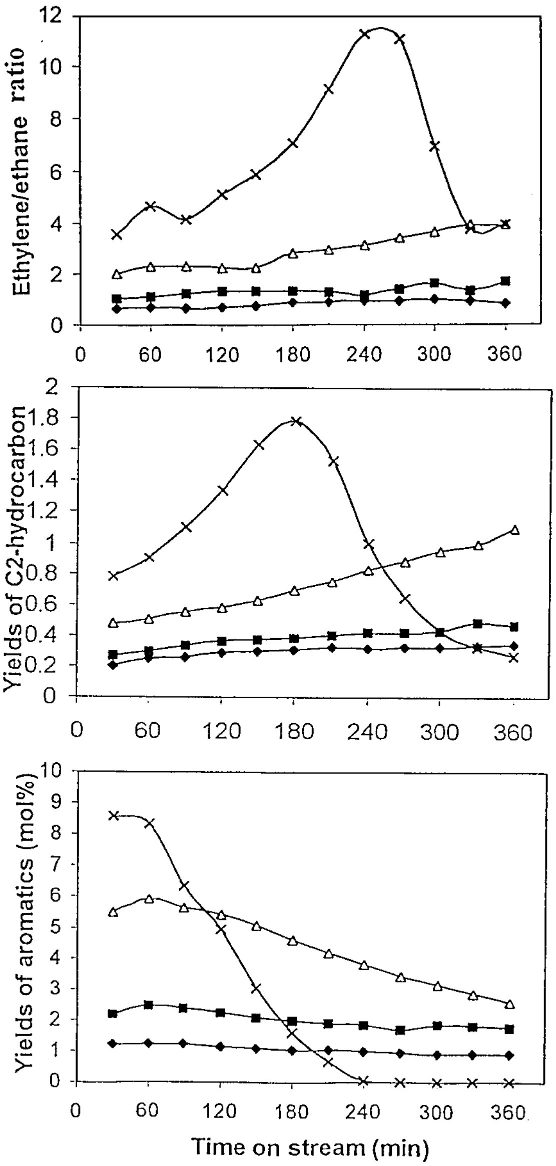

Figure 1. Catalytic performance of 2 wt% Mo/HZSM-5 catalyst as a function of reaction temperature (T_r): (◆) 600 °C, (■) 650 °C, (△) 700 °C, (×) 770 °C.

adsorbed at acidic Si–OH–Al groups [21,22]. The component at 225 °C has been attributed to NH_3 weak adsorption on Brønsted acid sites [22] as well as NH_3 association with extra framework Al [23] or Si–OH

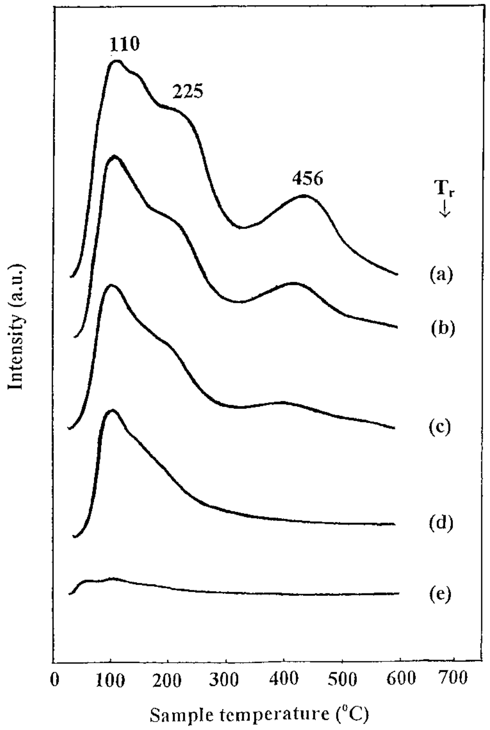

Figure 2. NH_3-TPD profiles of 2 wt% Mo/HZSM-5 (a) fresh, and after on-stream reaction at (b) 600 °C, (c) 650 °C, (d) 700 °C, and (e) 770 °C.

[24]. A reaction time of 6 h at $T_r = 600\,°C$ did not cause a significant change in the acidic property. However, with a rise in reaction temperature from 600 to 770 °C, the amount of surface Brønsted acid sites diminished as reflected in intensity reduction at 225 and 456 °C; at $T_r = 770\,°C$, all the signal intensities reached zero background level (figure 2). A similar trend of diminution was observed with surface area and pore volume (table 2). At $T_r = 770\,°C$, the decreases in surface area and pore volume were *ca.* 90.1% and 72.2%, respectively. Surface Mo species have been suggested to be responsible for C–H bond activation [10,12,14] and initial C–C bond formation [14], whereas surface acid sites located mainly in the channels of zeolite [25] to be responsible for C_2-hydrocarbon oligomerization and cyclization [10,12,14]. Based on such an understanding, one can envision that coke formation firstly occurred on the acid sites, resulting in a decrease in the amount of Brønsted acid sites and a

Table 2
BET surface area, pore volume and average pore size of used Mo/HZSM-5 catalysts[a]

T_r (°C)	O_2 (vol%)	Surface area (m^2/g)	Pore volume (ml/g)	Average pore size (nm)
fresh	—	319.7	0.20	2.4
600	—	250.3	0.16	2.6
650	—	198.1	0.13	2.7
700	—	187.7	0.12	2.7
770	—	31.6	0.05	6.3
770 (black zone)	5.3	171.2	0.12	2.9
770 (gray zone)	5.3	261.8	0.18	2.6

[a] After 6 h of reaction.

Table 3
Effects of reaction temperature (T_r) on methane aromatization in the presence of O_2 [a]

T_r (°C)	O_2 (vol%)	Conv. (mol%)		Selectivity (mol%)							$C_2H_4:C_2H_6$
		CH_4	O_2	CO	CO_2	C_2H_4	C_2H_6	C_6H_6	C_7H_8	$C_{10}H_8$	
600	1.5[b]	~0.0	—	—	—	—	100.0	—	—	—	—
	1.5	1.0	100	68.3	26.0	2.7	3.0	—	—	—	0.9 : 1
650	1.5[b]	0.1	—	—	—	—	100.0	—	—	—	—
	1.5	1.0	100	72.7	17.8	2.6	6.9	—	—	—	0.4 : 1
700	1.5[b]	0.1	—	—	—	—	100.0	—	—	—	—
	1.5	4.4	100	74.6	—	8.6	1.1	15.7	—	—	7.8 : 1
	2.1	1.3	100	73.6	21.8	2.2	2.4	—	—	—	0.9 : 1
770	1.5[b]	0.2	—	—	—	12.7	87.3	—	—	—	0.1 : 1
	1.5	10.9	100	26.6	—	5.3	1.4	55.0	1.7	11.0	3.7 : 1
	2.1	11.5	100	35.4	—	3.4	1.3	48.9	1.4	9.6	2.6 : 1
	3.2	13.1	100	48.5	—	2.7	1.2	38.9	1.2	7.5	2.2 : 1
	5.3	17.4	100	61.8	—	3.3	1.1	28.3	0.8	4.7	3.0 : 1
	8.4	6.0	100	77.5	19.8	1.2	1.5	—	—	—	0.8 : 1
	20.2	13.6	100	68.2	31.2	0.2	0.4	—	—	—	0.5 : 1

[a] Data were recorded *ca.* 2 h after the start of the reaction.

[b] Blank.

decrease in pore volume of zeolite. The result is a suppression in C_2-hydrocarbon oligomerization and cyclization but an increase in C_2-hydrocarbon yield and C_2H_4/C_2H_6 ratio. Further coking on Mo sites would subsequently lead to deactivation of the catalyst for methane dehydrogenation and a drastic decrease in C_2-hydrocarbon yield.

The effect of co-feeding 1.5 vol% of O_2 on methane aromatization over 2 wt% Mo/HZSM-5 catalyst is summarized in table 3. After a reaction time of 2 h in a blank reactor, CH_4 and O_2 conversions were low (<0.3%); there was only a small amount of C_2-hydrocarbon (mainly ethane) produced. In the presence of Mo/HZSM-5, both methane and oxygen conversions increased considerably. At $T_r = 600$ or 650 °C, methane conversion was *ca.* 1.0%, whereas oxygen conversion was 100%; besides CO, CO_2 and H_2O (the predominant products), there was 6–9% of C_2-hydrocarbon (mainly ethane) but no detection of aromatics and hydrogen. At $T_r = 700$ °C, the selectivities of aromatics, C_2-hydrocarbon, and CO were 15.7%, 9.7%, and 74.6%, respectively, and methane conversion was 4.4%. As T_r was raised to 770 °C, methane conversion was 10.9% and aromatics selectivity reached 56.3%, whereas CO selectivity decreased to 26.6%. We observed that at $T_r = 700$ °C or higher, CO was the only detectable oxygen-containing product and ethylene was the main C_2-hydrocarbon. With an O_2 concentration of 2.1 vol%, there was no detection of aromatics at $T_r \leq 700$ °C, whereas at $T_r = 770$ °C, aromatics (selectivity, 49.0%) and CO (selectivity, 35.4%) were observed. Further rise in O_2 concentration at $T_r = 770$ °C would result in a decrease in aromatics selectivity but an increase in CO selectivity. At 8.4 vol% oxygen, methane conversion was 6.0% and the products were CO, CO_2, H_2O, H_2 and C_2-hydrocarbons (mainly ethane); there was no aromatics detection. At 20.2 vol% oxygen, neither aromatics nor H^2 was detected. The results illustrated the O_2/CH_4 ratio suitable for methane oxidative aromatization over 2 wt% Mo/HZSM-5 at 770 °C was higher than that at 700 °C.

Illustrated in figure 3 is the effect of oxygen (1.5–5.3 vol%) on methane aromatization at 770 °C over 2 wt% Mo/HZSM-5 during 6 h of on-stream reaction. At 1.5 vol% oxygen, the early drop in aromatics yield at 0 vol% oxygen was substantially moderated and an aromatics yield of *ca.* 7% could be retained for 150 min. With further rise of oxygen concentration to 5.3 vol%, the initial aromatics yield decreased slightly, whereas catalyst durability improved. At 3.2 vol% oxygen, the catalyst could last for more than 6 h with an aromatics yield of 4.3%. With the addition of 1.5–5.3 vol% of oxygen, and compared to the situation of 0 vol% oxygen, the C_2-hydrocarbon yield was lower and the CO yield higher.

During the oxidative reaction of methane (oxygen concentration, 1.5–5.3 vol%), we observed that the section of catalyst bed close to the gas inlet was gray, whereas that close to the outlet was black. The catalytic materials of these sections exhibited different losses in surface area, pore volume (table 2), and changes in acid property (figure 4) as compared to those of a fresh sample. Losses in the black region are mainly due to coke deposition, whereas those in the gray region are due to Mo species dispersion and zeolite dealumination. The existence of different reaction zones in the catalyst bed is also supported by the results of XPS studies (figure 5). After reaction at 5.3 vol% oxygen and 770 °C, the Mo $3d_{5/2}$ peak of the gray material was at a binding energy (BE) of 233.0 eV, and was assigned to

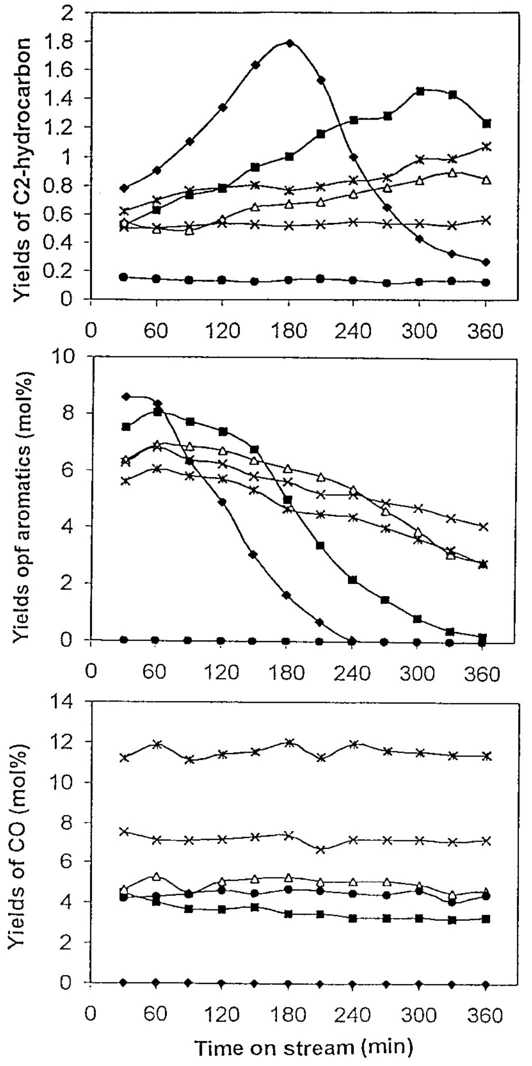

Figure 3. Effects of oxygen on methane aromatization over 2 wt% Mo/HZSM-5 at 770 °C; O_2 content: (◆) 0 vol%, (■) 1.5 vol%, (△) 2.1 vol%, (×) 3.2 vol%, (✱) 5.3 vol%, and (●) 8.4 vol%.

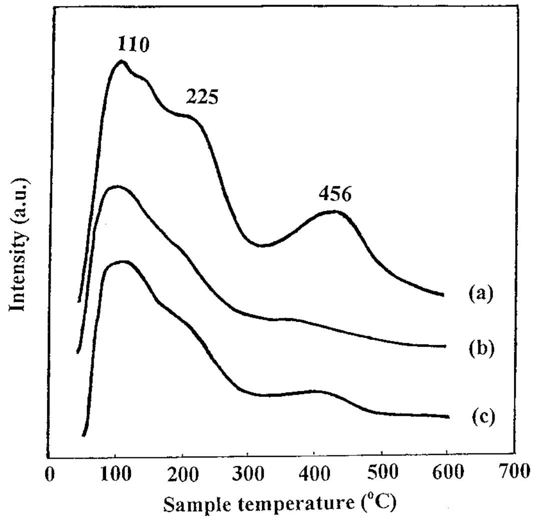

Figure 4. NH_3-TPD profiles of 2 wt% Mo/HZSM-5 (a) fresh, and used catalyst collected at (b) black zone and (c) gray zone after on-stream reaction at 770 °C.

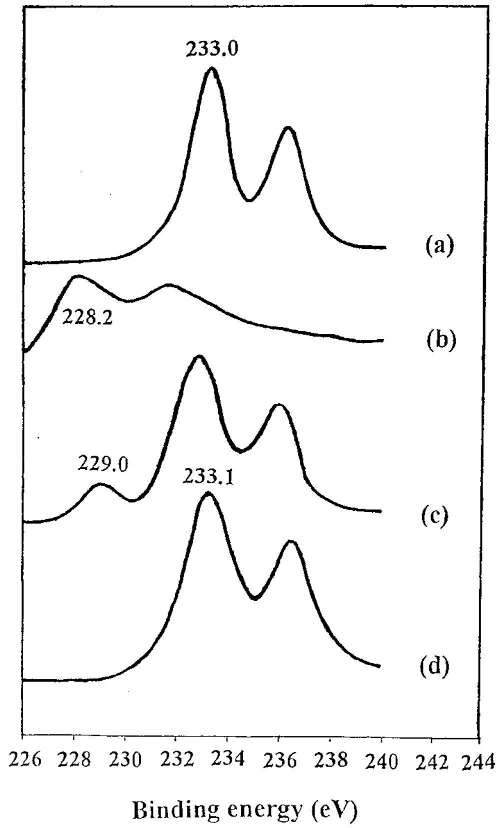

Figure 5. Mo 3d XPS spectra of used Mo/HZSM-5 catalysts after 1.5 h of reaction: (a) gray zone, 5.3 vol% O_2; (b) black zone, 5.3 vol% O_2, sample was reduced with hydrogen at 600 °C for 2 h before test; (c) 8.4 vol% O_2; (d) 20.2 vol% O_2.

Mo^{6+}; for the black material, the BE value for Mo $3d_{5/2}$ was registered at 228.2 eV, and the C 1s peak at 283.6 eV, implying the formation of Mo_2C, an active species for methane aromatization [12,13]. At an oxygen content of 8.4 vol% or 20.2 vol%, there was no obvious difference in color in the catalyst bed. At 8.4 vol% oxygen, there were three Mo 3d components at 229.0, 232.8 and 235.8 eV, implying the co-existence of Mo^{4+}, Mo^{5+}, and Mo^{6+} [11]. At 20.2 vol% oxygen, molybdenum was found to be mainly in the form of Mo^{6+} and the Mo 3d doublets were at 233.1 and 236.2 eV.

The gas hourly space velocity of methane exerted significant influences on the reaction performance of methane conversion. Table 4 and figure 6 showed the distribution of products over Mo/HZSM-5 at various catalyst contents at 770 °C, 34 ml min^{-1}, and 5.3 vol% oxygen after 2 h of reaction. Over 0.05 g or 0.1 g Mo/HZSM-5, O_2 was completely consumed and CO, CO_2, and H_2O were the predominant products; we detected a small amount of C_2-hydrocarbon (mainly ethane) but no aromatics and H_2. At a catalyst content of 0.3 g, H_2 was produced but there was still no aromatics detection; there was a slight increase in CO and CO_2 yields but a decrease in H_2O yield. At 0.5 g Mo/HZSM-5, we observed 0.4% benzene yield, 10.6% CO yield, a trace

Table 4
Products found in methane aromatization over 2 wt% Mo/HZSM-5 in the presence of oxygen or nitric oxide at 770 °C for 2 h

Catalyst (g)	O_2 (vol%)	NO (vol%)	Products found							
0.05	5.3	—	CO	CO_2	—	H_2O	C_2H_4	C_2H_6	—	—
0.10	5.3	—	CO	CO_2	—	H_2O	C_2H_4	C_2H_6	—	—
0.30	5.3	—	CO	CO_2	H_2	H_2O	C_2H_4	C_2H_6	—	—
0.30	3.2	—	CO	—	H_2	—	C_2H_4	C_2H_6	Aromatics	—
0.50	5.3	—	CO	CO_2	H_2	—	C_2H_4	C_2H_6	Aromatics	—
1.00	5.3	—	CO	—	H_2	—	C_2H_4	C_2H_6	Aromatics	—
0.20	—	9.1	CO	CO_2	H_2	H_2O	C_2H_4	C_2H_6	—	N_2
0.20	—	5.6	CO	—	H_2	—	C_2H_4	C_2H_6	Aromatics	N_2
1.00	—	9.1	CO	—	H_2	—	C_2H_4	C_2H_6	Aromatics	N_2

Aromatics include C_6H_6, C_7H_8 and $C_{10}H_8$.

of CO_2 (less than 0.1% yield) and no H_2O. At 1.0 g, the yield of aromatics and CO increased to 5.9% and 11.2%, respectively, and there was no CO_2 and H_2O formation.

According to the above results, we suggested that at $T_r = 770\,°C$ and $34\,ml\,min^{-1}$ with oxygen ≤ 5.3 vol%, there were three different reaction regions in the catalyst bed (figure 7): (i) methane oxidation; (ii) methane reforming; and (iii) methane aromatization. At the gray oxidation region, methane was converted mainly to CO_x and H_2O; a certain amount of C_2-hydrocarbon was produced probably *via* an intermediate product such as methanol [5,8,9]. In addition, with the presence of MoO_3, the oxidative coupling reaction of methane also occurred. At the reforming region, CO, CO_2, and H_2 were formed *via* the $CH_4 + H_2O = CO + 3H_2$ and $CO + H_2O = CO_2 + H_2$ reactions; carbon dioxide was then converted to CO and H_2 *via* the $CO_2 + CH_4 = 2CO + 2H_2$ reaction. The reduction of a certain amount of molybdenum oxide in the reforming zone is probably due to H_2. The existence of carbon dioxide in the oxidation and reforming zones would result in a suppression of surface active carbon species, possibly in the form of molybdenum carbide, and the generation of aromatic compounds such as benzene and naphthalene became impossible [18]. With the presence of CO and H_2, dehydro-aromatization of methane occurred in the black aromatization region. It should be noted that the distribution of these three reaction regions was affected by oxygen concentration and/or reaction temperature. With a rise in oxygen concentration or a decrease in reaction temperature, the oxidation and reforming regions enlarged, while the aromatization region contracted or even disappeared at higher oxygen levels (*e.g.*, 8.4 vol% at $T_r = 770\,°C$).

Nitric oxide decomposes over transition metal ions/ZSM-5 zeolite to N_2 and O_2; in the presence of methane or other light hydrocarbons at elevated temperature, there would be H_2O and CO_x formation [5,26]. We observed that the catalytic stability for methane dehydro-aromatization at 770 °C over 2 wt% Mo/HZSM-5 was

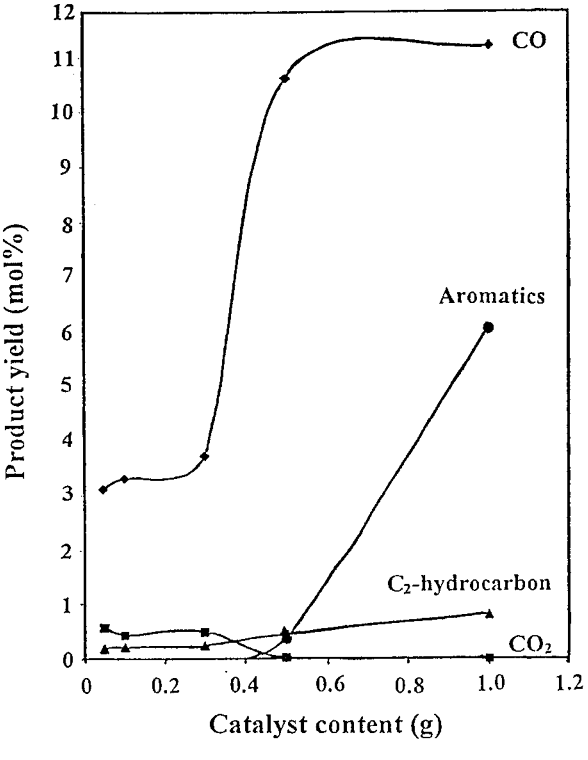

Figure 6. Catalytic performance of 2 wt% Mo/HZSM-5 at various catalyst contents (reaction condition: 770 °C and $34\,ml\,min^{-1}$): (◆) CO, (●) aromatics, (▲) C_2-hydrocarbon, and (■) CO_2.

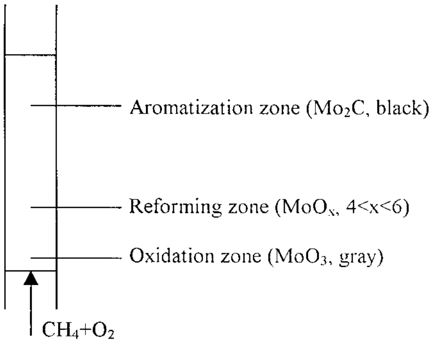

Figure 7. Schematic illustion of the three different regions in the Mo/HZSM-5 catalyst bed (1.0 g) observed after an on-stream time of 6 h at 770 °C (oxygen concentration, 1.5–5.3 vol%).

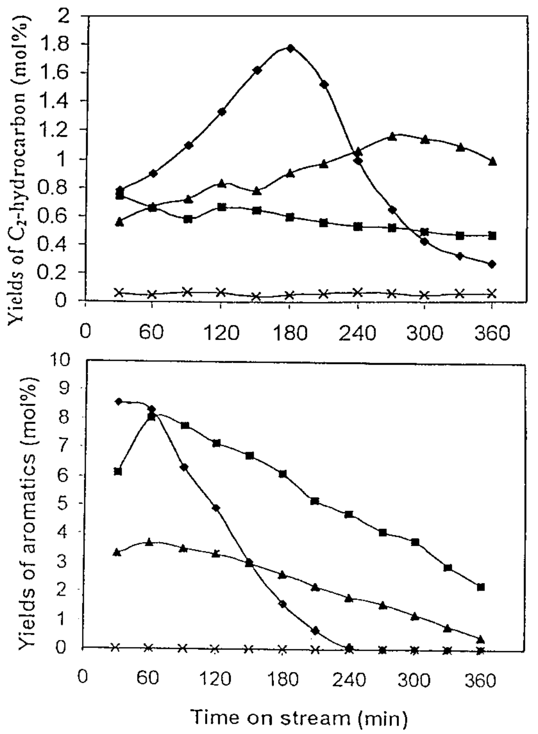

Figure 8. Effect of nitric oxide on methane aromatization over 2 wt% Mo/HZSM-5 at 770 °C; NO content: (◆) 0 vol%, (■) 5.6 vol%, (▲) 9.1 vol%, and (×) 14.2 vol%.

improved by adding 5.6 vol% nitric oxide to the methane feed (figure 8), and aromatics yield remained above 6% for 150 min. At a nitric oxide concentration of 9.1 vol%, aromatics yield decreased by *ca.* 3% and there was a considerable increase in C_2-hydrocarbon yield (figure 8). The suppression of ethylene oligomerization and cyclization could be due to the formation of nitrogen-containing entities at acid sites, a result of NO interaction with methane or other hydrocarbons as reported by Buckles and Hutchings [27]. At 14.2 vol% nitric oxide, there was no aromatics formation. Since the product distribution over Mo/HZSM-5 varied with catalyst contents (table 4), we suggested that there were also different reaction zones in the catalyst bed.

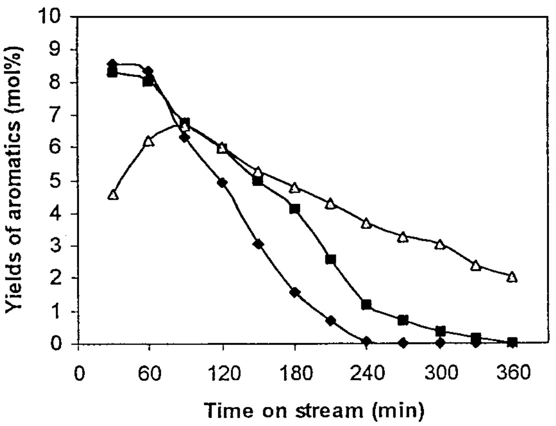

Figure 9. Effect of hydrogen on methane aromatization over 2 wt% Mo/HZSM-5 at 770 °C; H_2 content: (◆) 0 vol%, (■) 5.6 vol%, and (△) 12.0 vol%.

It is apparent that the adding of a suitable amount of oxygen ($\leq$5.3 vol%) or NO ($\leq$9.1 vol%) is beneficial to catalyst stability. Yuan *et al.* [19] suggested that such an improvement was due to the partial removal of surface coke species. We observed that at an oxygen content of 5.3 vol%, there was complete oxygen conversion to CO_x and H_2O over 0.05 g of Mo/HZSM-5 catalyst; in other words, there was no oxygen left for the removal of coke in the region of methane aromatization. We have proved that CO and H_2 can be generated in the partial oxidation of methane over Mo/HZSM-5. Ohnishi *et al.* [18] have reported that in methane aromatization over Mo/HZSM-5, a few percent of carbon monoxide in the methane feed would promote benzene production and significantly improve the stability of the catalyst. The unique role of CO addition was based on the formation of C and CO_2 in CO disproportionation (Boudart reaction); the former hydrogenated to active carbon species [CH_x] and involved in aromatics production, while the latter reacted with inert surface carbon species to regenerate CO. A suitable amount of CO_2 exhibited similar effects due to CO generation in CO_2/CH_4 reforming [18]. In addition, as illustrated in figure 9, the presence of hydrogen is beneficial to catalyst stability. We deduce that both H_2 and CO generated in the process were responsible for the improved stability of Mo/HZSM-5.

4. Conclusions

A 2 wt% Mo/HZSM-5 catalyst for methane aromatization deactivated after 4 h of non-oxidative reaction (temperature = 770 °C, space velocity = 34 ml min^{-1}) due to severe coking. With a suitable amount of O_2 ($\leq$5.3 vol%) or NO ($\leq$9.1 vol%) in the feed, the catalyst could last for more than 6 h at 770 °C. Depending on oxygen concentration or reaction temperature, there were three reaction regions in the catalyst bed: (i) methane oxidation; (ii) methane reforming; and (iii) methane aromatization. The hydrogen and carbon monoxide generated *via* the reforming of methane are considered to be responsible for the improved performance of the catalyst. With a rise in O_2 ($\geq$8.4 vol%) or NO ($\geq$14.2 vol%) concentration, the aromatization region disappeared; CO and CO_2 were the predominant carbon-containing products.

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