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Methane aromatization over 2wt% Mo/HZSM-5 in the presence of O₂ and NO

Abstract In the non-oxidative aromatization reaction (temperature=750°C, flow rate =34 ml min⁻¹), 2wt% Mo/HZSM-5 deactivated after 4 h due to severe coking. We observed that with a suitable amount of O₂ (≤5.3vol%) in the methane feed, the catalyst could last for more than 6 h with a *ca.* 4% yield of aromatics at 750°C. Depending on concentration of O₂ or reaction temperature, there are three reaction zones in the catalyst bed: (i) methane oxidation, (ii) methane reforming, and (iii) methane aromatization. CO and H₂ 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 O₂ (≥8.4vol%) or NO (≥14.2vol%) concentration would result in CO and CO₂ being the predominant carbon-containing products; C₂H₄ and C₂H₆ were generated in small amounts and no aromatics were detected.

Keywords: methane aromatization, Mo/HZSM-5, oxygen 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 dehydro-aromatization in the presence of an oxidant, especially oxygen, is of particular interest.

By using a mixture of methane and oxygen (CH₄:O₂:N₂=10:1:4), Claridge *et al* [1] obtained 13.2% methane conversion and 23.4% aromatics selectivity (yield=3.1%) over NaCl/MnO₂ at 950°C and at an elevated pressure of 6 atm. Earlier, Otsuka *et al* [2] have 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 C₂₊ 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 La₂O₃+Mo/HZSM-5; the reaction condition adopted were CH₄+O₂ (6:1 mole ratio) at 750°C and 3500 ml h⁻¹. In these cases, ethylene, ethane or methyl radical (CH_x•) 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 (C₅₊) directly from methane and oxygen over HZSM-5 was first reported by Shepelev and Ione [4] but the results was 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 C₅₊ 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 dehydro-aromatization of methane [10-17]; despite of 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; only a yield of *ca.* 0.2% at 750°C and 3500 ml h⁻¹ [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 7vol% at 700, 750 and 800°C, respectively. Our present work is to investigate further the effects of oxygen additions on methane dehydrogenation and aromatization over 2wt% Mo/HZSM-5.

2. Experimental

Catalyst preparation

The 2wt% Mo/HZSM-5 catalyst was prepared by impregnating HZSM-5 (Si/Al=25, Nankai University, P.R.China) with a desired amount of ammonium heptamolydate 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.

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 CH₄ + O₂ (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 CH₄, CO, CO₂ and other light hydrocarbons. A 5A Molecular Sieve column was used for the separation of H₂, O₂ and N₂. Methane conversion and product selectivity were calculated on a carbon number basis.

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 NH₃ 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 to

room temperature in He before being exposed to a NH₃/He mixture of 8 vol% ammonia for 30 min. After NH₃ 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 K α 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 2wt% 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% CH₄ conversion, 1.3% aromatics yield, and 0.2% C₂-hydrocarbon (C₂H₄/C₂H₆ ratio=0.7:1) yield at T_r =600°C. With a rise in T_r from 600 to 750°C, the methane conversion, C₂-hydrocarbon and aromatics yields as well as C₂H₄/C₂H₆ ratio increased. At T_r =750°C, 9.3% methane conversion, 8.4% aromatics and 0.9% C₂-hydrocarbon yields were obtained; the C₂H₄/C₂H₆ ratio reached 4.6:1. Apparently, a rise in T_r from 650 to 750°C was beneficial not only for methane activation but also for the oligomerization and cyclization of ethylene to aromatics.

Shown in Fig. 1 is the catalytic performance of 2wt% 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 C₂-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 C₂-hydrocarbon yield from 0.5% to 1.1%. At T_r =750°C, the catalyst deactivated for aromatization after *ca.* 4h; the C₂-hydrocarbon yield and the C₂H₄/C₂H₆ ratio first increased and then drastically decreased. The highest C₂-hydrocarbon yield was *ca.* 1.8% after 3h.

Coke deposition is considered to be the main cause for the gradual deactivation of Mo/HZSM-5 in methane nonoxidative aromatization [18-20]. Fig. 2 shows the NH₃-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 NH₃ whereas the one at 456°C to NH₃ strongly adsorbed at acidic Si-OH-Al groups [21, 22]. The component at 225°C has been attributed to NH₃ weak adsorption on Brønsted acid sites [22] as well as NH₃ association with extra framework Al [23] or Si-OH [24]. A reaction time of 6 h at T_r=600°C did not cause a significant change in acidic property. However, with a rise in reaction temperature from 600 to 750°C, the amount of surface Brønsted acid sites diminished as reflected in intensity reduction at 225 and 456°C; at T_r=750°C, all the signal intensities reached zero background level (Fig. 2). A similar trend of diminution was observed with surface area and pore volume (Table 2). At T_r=750°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 C₂-hydrocarbon oligomerization and cyclization [10, 12, 14]. Based on such an understanding, one can envision that coke formation at the acid sites would suppress oligomerization and cyclization, resulting in a decrease in aromatics yield but increases in C₂-hydrocarbon yield and C₂H₄/C₂H₆ ratio. Further coking on Mo sites would subsequently lead to the deactivation of catalyst for methane dehydrogenation and a drastical decrease in C₂-hydrocarbon yield.

The effect of co-feeding 1.5vol% of O₂ on methane aromatization over 2wt% Mo/HZSM-5 catalyst is summarized in Table 3. After a reaction time of 2 h in a blank reactor, CH₄ and O₂ conversions were low (<0.3%); there was only a small amount of C₂-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, CO₂ and H₂O (the predominant products), there was 6-9% of C₂-

hydrocarbon (mainly ethane) but no detection of aromatics and hydrogen. At $T_r=700^\circ\text{C}$, 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 750°C , methane conversion was 10.9% and aromatics selectivity reached 56.3%, whereas CO selectivity decreased to 26.6%. We observed that at $T_r=700^\circ\text{C}$ or higher, CO was the only detectable oxygen-containing product and ethylene was the main C_2 -hydrocarbon. With an O_2 concentration of 2.1vol%, there was no detection of aromatics at $T_r\leq 700^\circ\text{C}$, whereas at $T_r=750^\circ\text{C}$, aromatics (selectivity, 49.0%) and CO (selectivity, 35.4%) were observed. Further rise in O_2 concentration at $T_r=750^\circ\text{C}$ would result in a decrease in aromatics selectivity but an increase in CO selectivity. At 8.4vol% 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 20.2vol% oxygen, neither aromatics nor H_2 was detected. The results illustrated the O_2/CH_4 ratio suitable for methane oxidative aromatization over 2wt% Mo/HZSM-5 at 750°C was higher than that at 700°C .

Illustrated in Fig. 3 is the effect of oxygen (1.5-5.3vol%) on methane aromatization at 750°C over 2wt% Mo/HZSM-5 during 6 h of on-stream reaction. At 1.5vol% oxygen, the early drop in aromatics yield at 0vol% oxygen was substantially moderated and an aromatics yield of *ca.* 7% could be retained for 150 min. With further rise of oxygen concentration to 5.3vol%, the initial aromatics yield decreased slightly, whereas catalyst durability improved. At 3.2vol% oxygen, the catalyst could last for more than 6 h with an aromatics yield of 4.3%. With the addition of 1.5 to 5.3vol% of oxygen, and compared to the situation of 0vol% oxygen, the C_2 -hydrocarbon yield was lower and the CO yield higher.

During the oxidative reaction of methane (oxygen concentration, 1.5-5.3vol%), 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 (Fig. 4) as compared to those of a fresh sample. The

existence of different reaction zones in the catalyst bed is also supported by the results of XPS studies (Fig. 5). After reaction at 5.3vol% oxygen and 750°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 Mo⁶⁺; for the black material, the BE value for Mo 3d_{5/2} were registered at 228.2 eV, and the C 1s peak at 283.6 eV, implying the formation of Mo₂C, an active species for methane aromatization [12, 13]. At an oxygen content of 8.4vol% or 20.2vol%, there was no obvious difference in color in the catalyst bed. At 8.4vol% oxygen, there were three Mo 3d components at 229.0, 232.8 and 235.8 eV, implying the co-existence of Mo⁴⁺, Mo⁵⁺, and Mo⁶⁺ [11]. At 20.2vol% oxygen, molybdenum was found to be mainly in the form of Mo⁶⁺ and the Mo 3d doublet 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 Fig. 6 showed the distribution of products over Mo/HZSM-5 at various catalyst contents at 750°C, 34 ml min⁻¹, and 5.3vol% oxygen after 2 h of reaction. Over 0.05 g or 0.1 g Mo/HZSM-5, O₂ was completely consumed and CO, CO₂, and H₂O were the predominant products; we detected a small amount of C₂-hydrocarbon (mainly ethane) but no aromatics and H₂. At a catalyst content of 0.3 g, H₂ was produced but there was still no aromatics detection; there was a slight increase in CO and CO₂ yields but a decrease in H₂O yield. At 0.5 g Mo/HZSM-5, we observed 0.4% benzene yield, 10.6% CO yield, a trace of CO₂ (less than 0.1% yield) and no H₂O. At 1.0 g, the yield of aromatics and CO increased to 5.9% and 11.2%, respectively; and there was no CO₂ and H₂O formation.

According to the above results, we suggested that at T_r=750°C and 34 ml min⁻¹ with oxygen ≤5.3vol%, there were three different reaction regions in the catalyst bed (Fig. 7): (i) methane oxidation, (ii) methane reforming, and (iii) methane aromatization. At the gray oxidation region, methane was converted mainly to CO_x and H₂O; C₂-hydrocarbon was produced probably via an intermediate product such as methanol [5, 8, 9]. In addition, with the presence of MoO₃, the oxidative coupling reaction of methane occurred. At the reforming region, CO, CO₂, and H₂ were formed via the CH₄ + H₂O = CO + 3H₂ and CO + H₂O = CO₂ + H₂ reactions; carbon dioxide was

then converted to CO and H₂ via the CO₂ + CH₄ = 2CO + 2H₂ reaction. The reduction of a certain amount of molybdenum oxide in the reforming zone is probably due to H₂. 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 H₂, 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. 8.4vol% at T_r=750°C).

Nitric oxide decomposes over transition metal ions/ZSM-5 zeolite to N₂ and O₂; in the presence of methane or other light hydrocarbons at elevated temperature, there would be H₂O and CO_x formation [5, 26]. We observed that the catalytic stability for methane dehydro-aromatization at 750°C over 2wt% Mo/HZSM-5 was improved by adding 5.6vol% nitric oxide to the methane feed (Fig. 8), and aromatics yield remained above 6% for 150 min. At a nitric oxide concentration of 9.1vol%, aromatics yield decreased by *ca.* 3% and there was a considerable increase in C₂-hydrocarbon yield (Fig. 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 14.2vol% 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.

It is apparent that the adding of a suitable amount of oxygen (≤5.3vol%) or NO (≤9.1vol%) 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 5.3vol%, there was complete oxygen conversion to CO_x and H₂O 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 H₂ 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 CO₂ 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 CO₂ exhibited similar effects due to CO generation in CO₂/CH₄ reforming [18]. In addition, as illustrated in Fig. 9, a presence of hydrogen is beneficial to catalyst stability. We deduce that both H₂ and CO generated in the process were responsible for the improved stability of Mo/HZSM-5.

4. Conclusion

A 2wt% Mo/HZSM-5 catalyst for methane aromatization deactivated after 4 h of non-oxidative reaction (temperature=750°C, space velocity =34 ml min⁻¹) due to severe coking. With a suitable amount of O₂ (5.3vol%) or NO (9.1vol%) in the feed, the catalyst could last for more than 6 h at 750°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 O₂ (8.4vol%) or NO (14.2vol%) concentration, the aromatization region disappeared; CO and CO₂ were the predominant carbon-containing products.

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

T_r (°C)	CH ₄ conversion (mol%)	Selectivity (mol%)					Yield (mol%)		C ₂ H ₄ :C ₂ H ₆
		C ₂ H ₄	C ₂ H ₆	C ₆ H ₆	C ₇ H 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
750	9.3	7.8	1.7	70.2	1.9	18.4	0.9	8.4	4.6 : 1

* data were recorded *ca.* 1 h after the start of the reaction; flow rate: 34 ml min⁻¹
C₂: C₂H₄ and C₂H₆

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

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
750	--	31.6	0.05	6.3
750 (black zone)	5.3	171.2	0.12	2.9
750 (gray zone)	5.3	261.8	0.18	2.6

* 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
750	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

Table 4 Products found in methane aromatization over 2wt% Mo/HZSM-5 in the presence of oxygen or nitric oxide at 750°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 $C_{10}H_8$

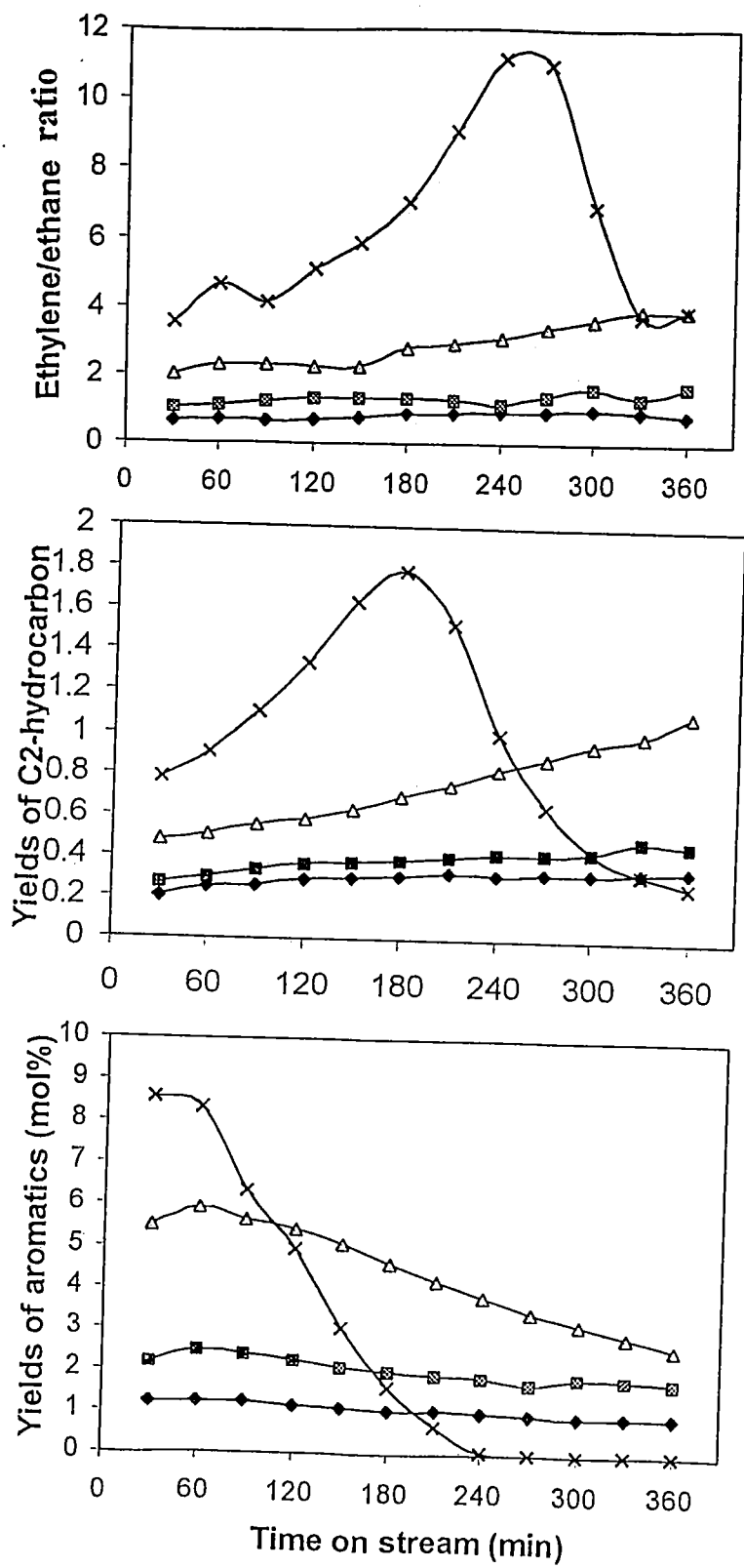


Fig. 1 Catalytic performance of 2wt% Mo/HZSM-5 catalyst as a function of reaction temperature (T_r): (◆) 600°C, (▣) 650°C, (Δ) 700°C, (×) 750°C

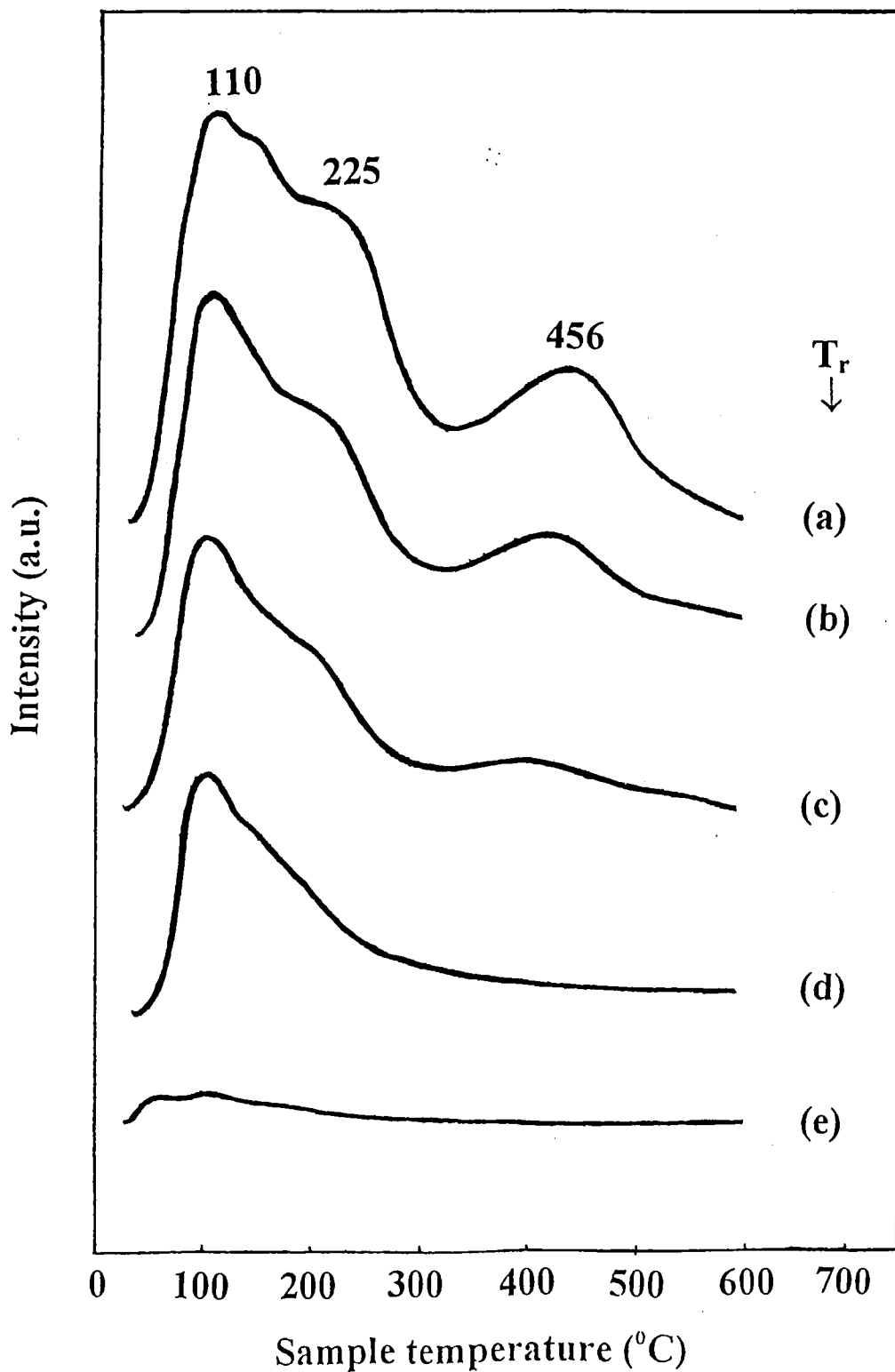


Fig. 2 NH₃-TPD profiles of 2wt% Mo/HZSM-5 (a) fresh, and after on stream reaction at (b) 600°C, (c) 650°C, (d) 700°C, and (e) 750°C.

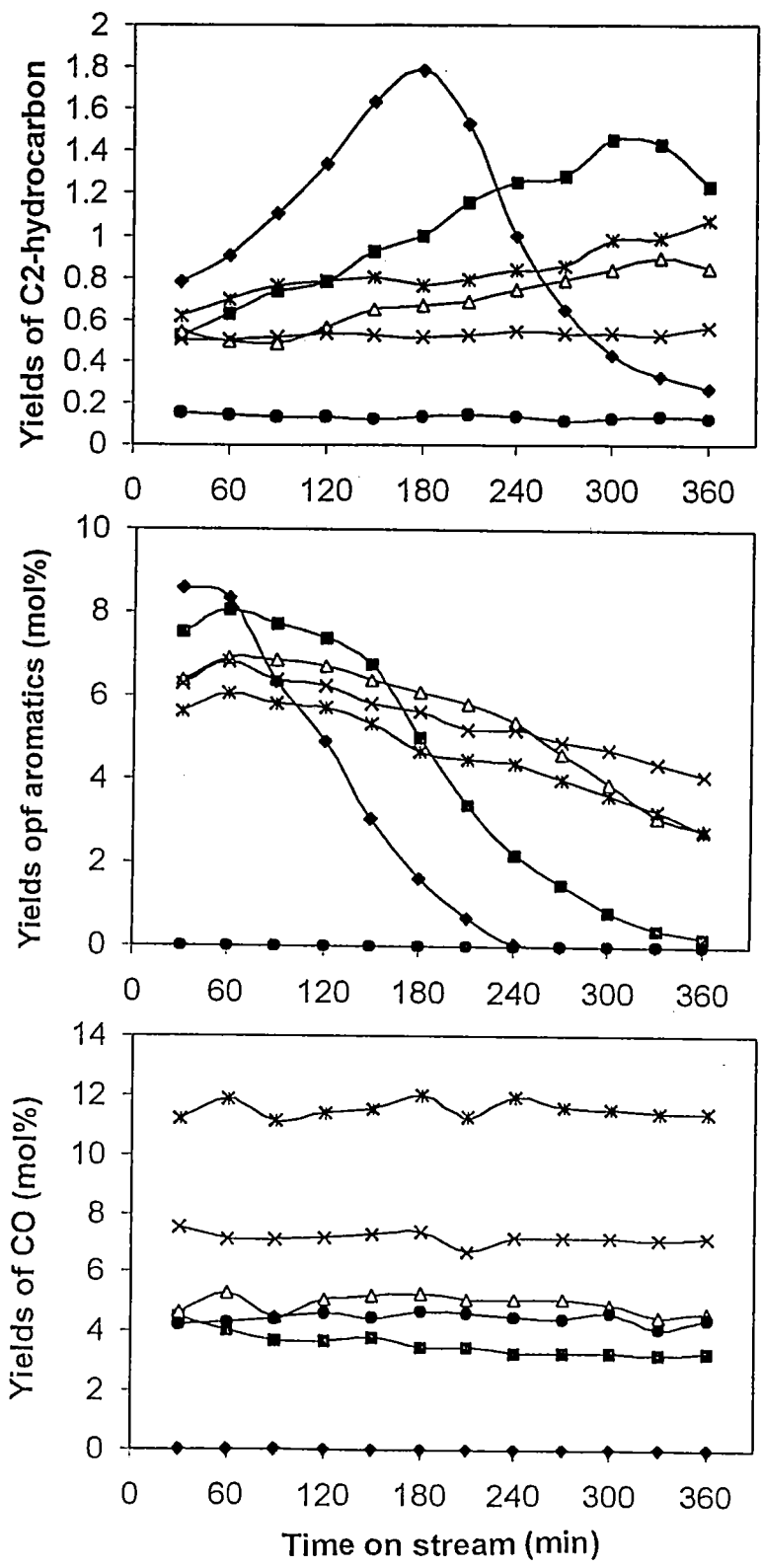


Fig. 3 Effects of oxygen on methane aromatization over 2wt% Mo/HZSM-5 at 750°C; O₂ content: (◆) 0vol%, (▣) 1.5vol%, (▲) 2.1vol%, (×) 3.2vol%, (*) 5.3vol%, and (●) 8.4vol%

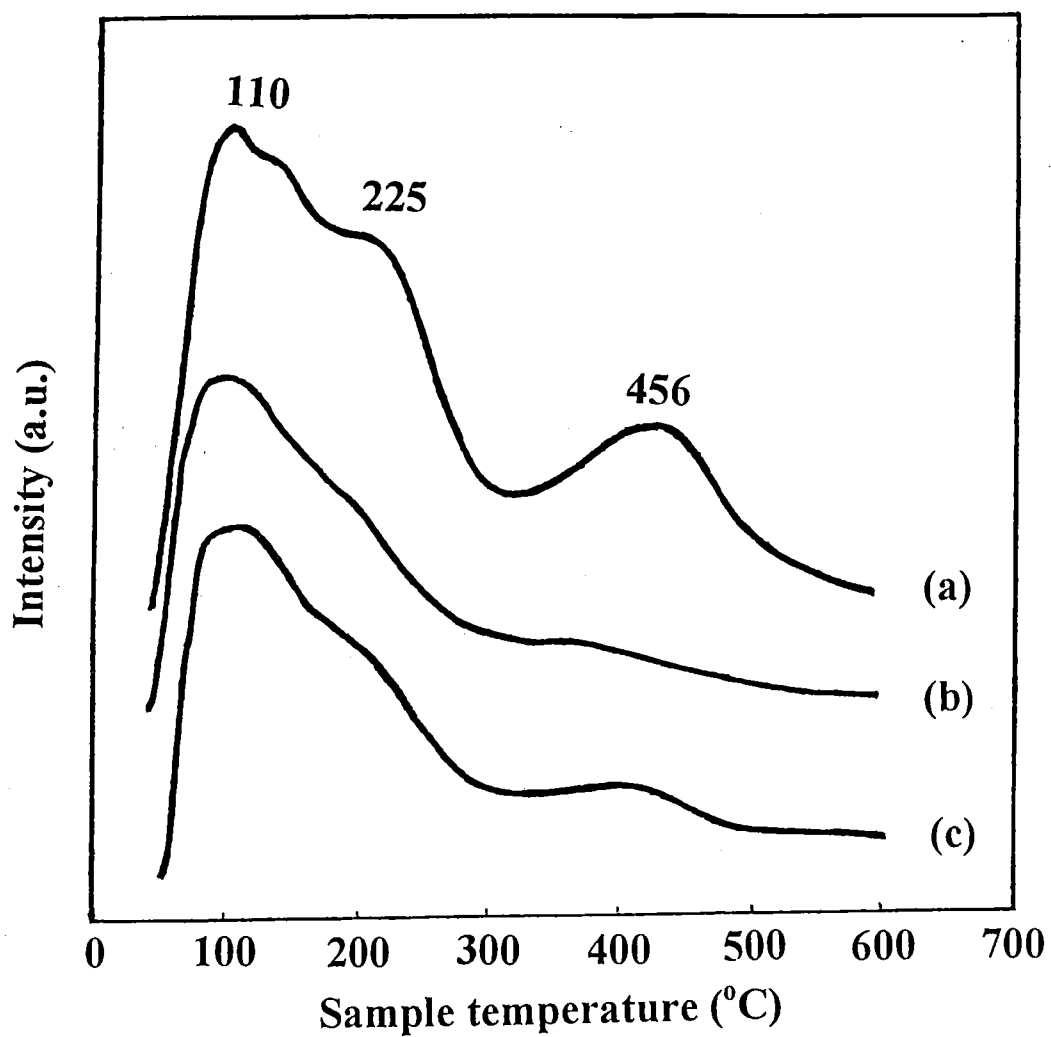


Fig. 4 NH₃-TPD profiles of 2wt% Mo/HZSM-5 (a) fresh, and catalyst collected at (b) black zone, and (c) gray zone after on-stream reaction at 750°C

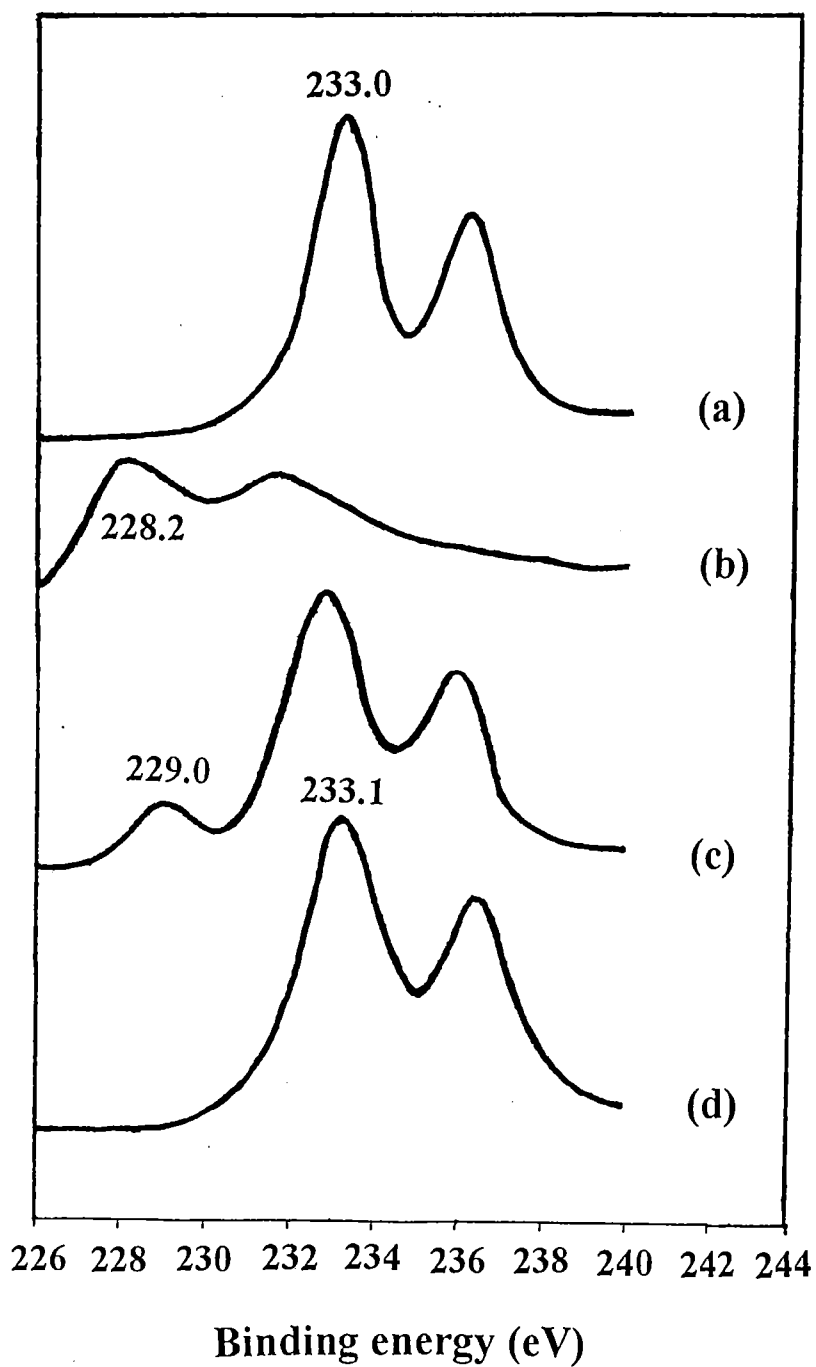


Fig. 5 XPS spectra of used Mo/HZSM-5 catalyst after 1.5 h of reaction. (a) gray zone, 5.3vol%O₂; (b) black zone, 5.3vol%O₂, Sample has been reduced with hydrogen at 600°C for 2 h before test; (c) 8.4vol%O₂; (d) 20.2vol%O₂

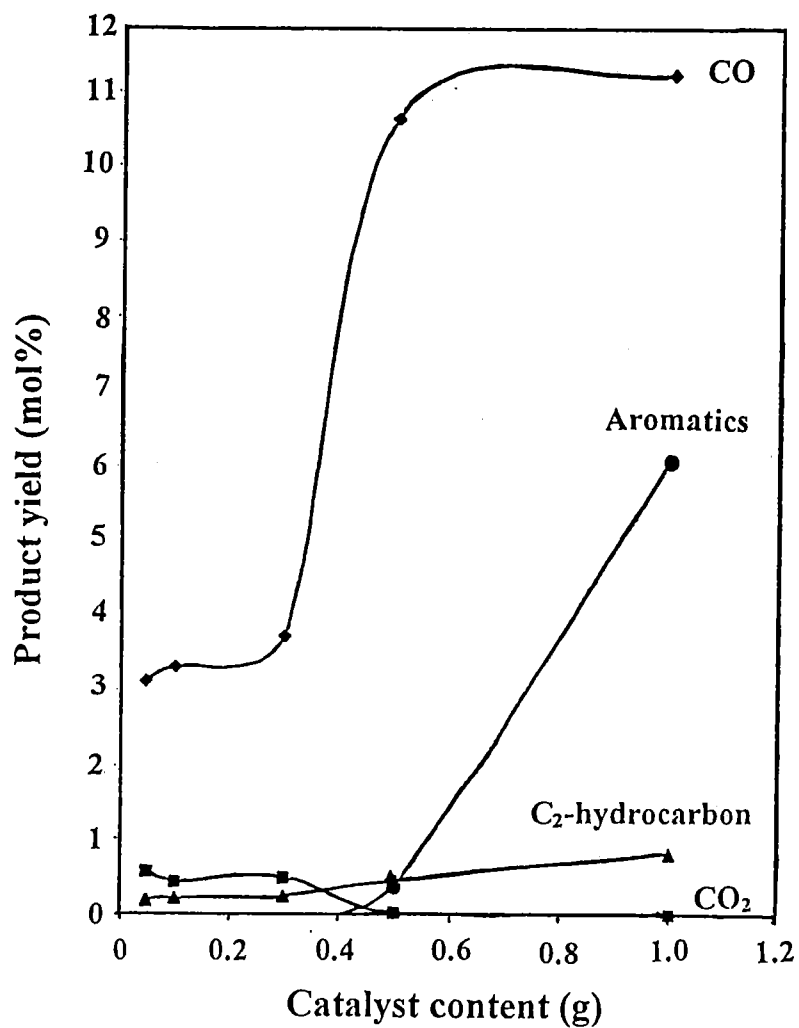


Fig. 6 Catalytic performance of 2wt% Mo/HZSM-5 at various catalyst contents (reaction condition: 750°C and 34 ml min⁻¹): (◆) CO, (●) Aromatics, (▲) C₂-hydrocarbon, and (■) CO₂.

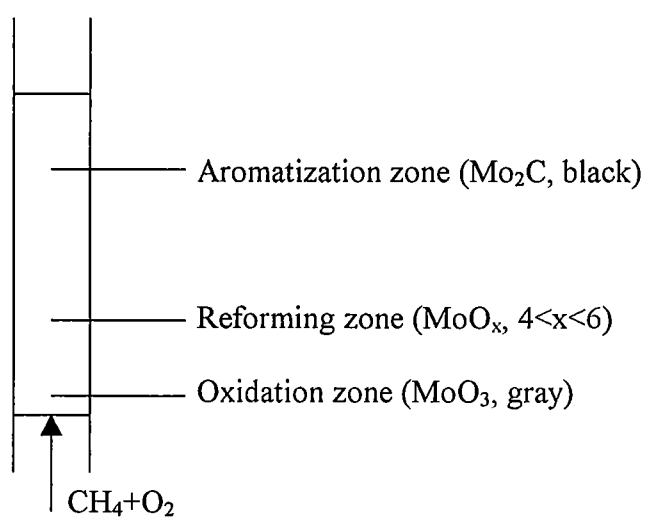


Fig. 7 Schematic illustration of the three different regions in the Mo/HZSM-5 catalyst bed (1.0g) observed after an on-stream time of 6 h at 750°C (oxygen concentration, 1.5-5.3 vol%)

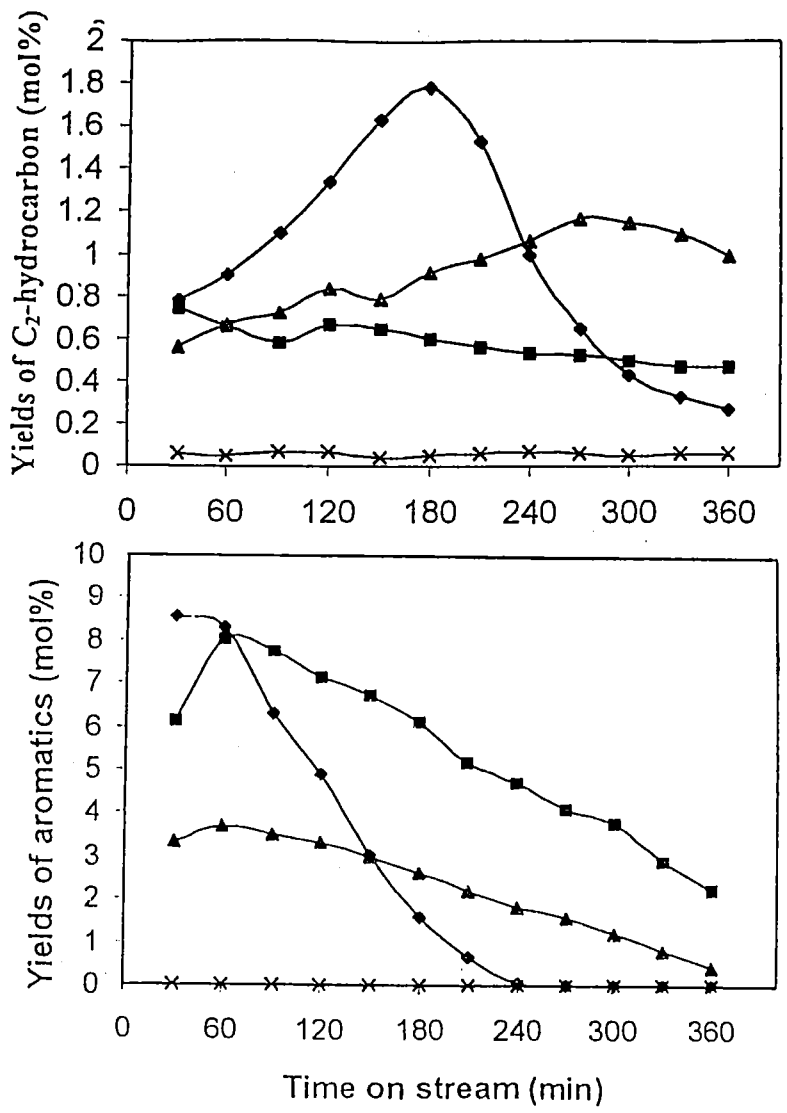


Fig. 8 Effect of nitric oxide on methane aromatization over 2wt% Mo/HZSM-5 catalyst at 750°C;

NO content: (◆) 0vol%, (■) 5.6vol%, (▲) 9.1vol%, and (×) 14.2vol%

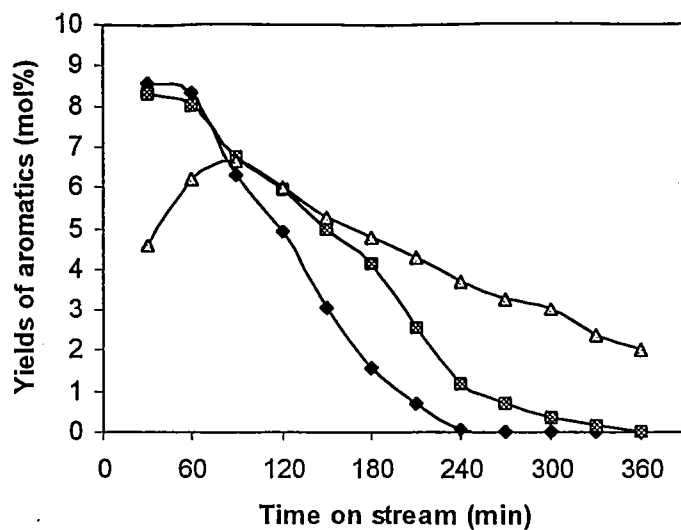


Fig. 9 Effect of hydrogen on the methane aromatization over 2wt% Mo/HZSM-5 catalyst at 750°C; H₂ content: (◆) 0vol%, (◻) 5.6vol%, and (Δ) 12.0vol%