Catalysis Letters Vol. 96, Nos. 3–4, July 2004 (© 2004)

CVD synthesis in static mode of Mo/H-ZSM5 catalyst for the methane dehydroaromatization reaction to benzene

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Received 28 January 2004; accepted 28 April 2004

Chemical vapor deposition (CVD) in a fused ampoule (static mode) was applied for synthesis of the series of Mo/H-ZSM5 catalysts. Kinetic data, TPO and EXAFS observation were evaluated in terms of effective dispersion of MoO_3 within the zeolite channels in 3% Mo/H-ZSM5 which provided an excellent activity and stability for methane dehydrocondensation reaction to benzene. The same catalyst doped with 0.5% La_2O_3 revealed significant suppression of coke and gave a little lower formation rate of benzene, probably due to formation of $La_2O_2CO_3$ species staying in equilibrium with gas phase of CO_2. $La_2O_2CO_3$ (Ia) phase formation was confirmed by X-ray diffraction experiment.

KEY WORDS: methane dehydroaromatization; Mo catalyst; CVD; stability; La_2O_3; $La_2O_2CO_3$.

1. Introduction

In future the direct catalytic dehydroaromatization of methane to benzene, naphthalene and hydrogen may open up many potential applications of natural gas, e.g. new process for synthesis of petrochemical feed stocks, hydrogen production for fuel cells and possible conversion of the methane hydrate (under the sea) or coal-bed methane to liquid fuels, chemicals and easily transported products. The process had been effectively improved by addition of a few percent CO/CO_2 to methane stream [1–3], dealumination treatment of zeolite [4], periodic switching treatment with H_2 and CO_2 [5] and silanation of external acid sites in H-ZSM5 [6]. Here we report a novel chemical vapor deposition (CVD) method where MoO_3 vapor was deposited on the H-ZSM5 in fused ampoule (static mode). By using this technique we hope to reduce the amount of MoO_3 and better control the parameters (e.g. balancing Brønsted acidity of zeolite) in preparation of catalyst comparing with conventional methods, e.g. physical mixing, wet impregnation or CVD in flowing system [7]. We decided to use CVD in static mode in viewpoint of pellet manufacturing process. Comparing with others preparation methods, e.g. impregnation, the CVD in static mode is simple two stage catalyst pellet manufacturing process from a fine powder (in our case Mo/H-ZSM5 powder) which can be directly compressed into the final form. Generally CVD methods remove the need for the complex recycling and disposal of solvents. In addition, possible recovery of unused MoO_3 precursor from flowing CVD system is possible after costly purifications, while novel CVD process effectively saves utilization of this substance.

Bimetallic Mo–La/H-ZSM5 catalyst was also prepared using the novel CVD, as mentioned. Doping lanthanum to Mo/H-ZSM5 was motivated by previous reports where this metal showed to be active for the oxidative coupling of methane [8] and exhibited interesting properties as a support for nickel catalyst used in dry reforming reaction of methane with CO_2, which was conducted at the same temperature range as the methane dehydroaromatization reaction [9,10].

2. Experimental

The series of Mo/H-ZSM5 samples were prepared in a glass reactor (figure 1) where H-ZSM5 (obtained from NH_4ZSM-5, $SiO_2/Al_2O_3 = 40$; Tosoh Co. after calcination at 773 K for 5 h) was loaded in large pocket and MoO_3 (Wako, 99.9% purity) in small one. The reactor was attached to a vacuum system and was evacuated up to 1.33 Pa. The precursor vapor (MoO_3) was directly interacted with pre-treated support (H-ZSM5) in the reactor by using following procedures: (1) the temperature of the Heated Zone I was raised from 293 to 723 K at a rate of 8 K/min and held there for 0.5 h, (2) the Heated Zone II was separated from the vacuum system by use of gas burner, (3) MoO_3 was transferred to the large pocket and was mixed with H-ZSM5 by shaking up together, and finally (4) the Heated Zone II was put into an oven, which was kept at 773 K for 5 h (in one case 2% Mo/H-ZSM5 was heated for 60 h). Prepared samples were designed as 1, 2, 3, 6, and 10-wt% Mo/H-ZSM5. Using procedure described above was prepared bimetallic catalyst 3Mo–0.5La wt%/H-ZSM5 by addition of

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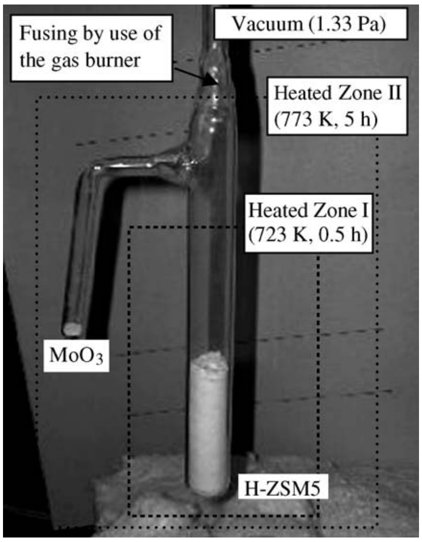

Figure 1. The equipment used for CVD preparation of Mo/H-ZSM5 catalysts in fused ampoule.

La_2O_3 (Wako, purity 99.99%). Additional 3% Mo and 10% Mo/H-ZSM5 was prepared from physical mixtures of MoO_3 and H-ZSM5. The mixture was grounded together for 15 min by using mortar and pestle. The resulting physical mixture was calcined at 773 K for 5 h in air.

According to the literature [11], the partial pressure of MoO_3 in air at 673 K is only about 10^{-6} Pa. It has been found by Xie and Tang [12] that a relatively low-melting-point oxide, such as MoO_3 (m.p. 1068 K, [13]), can disperse onto the surface of γ-Al_2O_3 as a monolayer either by heating or impregnation method. When a mixture of MoO_3 and γ-Al_2O_3 is heated at 723 K for 24 h, crystalline MoO_3 will disperse onto the surface of γ-Al_2O_3 to form a monolayer. In case, a high melting-point oxide, such as lanthanum oxide (m.p. 4473 K, [13]), cannot disperse on the surface of zeolite by simple heat-treatment. So it is expected that Mo–La/H-ZSM catalyst can be characterized as a physical mixture in viewpoint of interaction between molybdenum and lanthanum. Ma *et al.* [14] revealed that Mo ions can migrate into the lattice channels of H-ZSM5 zeolites. The process is accompanied by substitution of the Brønsted H atoms by Mo ions. According to these data, it is expected that MoO_3 migrates on the surface of zeolite under condition of Mo/H-ZSM5 preparation by CVD in static mode (at 773 K and 1.33 Pa), while La_2O_3 rather not.

The methane dehydrocondensation reaction was carried out in a fixed-bed continuous-flow system at 998 K, under a methane flow rate of 15 mL $\cdot$ min^{-1} (methane space velocities of 2500 mL g^{-1} h^{-1}) with 2% CO_2 at a pressure of 3×10^5 Pa. All the products were analyzed on-line by two GCs with FID and TCD, as described elsewhere [15]. The procedure of product analysis and kinetic measurements as well as coke formation was described in [2]. We use the internal standard method for the calculation of formation rate of reaction product including coke. Argon was used as an internal standard.

Mo K-edge XAFS (X-ray absorption fine structure) measurements were conducted on samples of Mo/H-ZSM5 at the Photon Factory of the National Laboratory for High Energy Physics (KEK-PF, Tsukuba, Japan) to characterize the Mo/H-ZSM5 prepared by CVD method. The energy and current of the electrons (or positions) were 2.5 GeV and 250 mA, respectively, and a Si(311) channel-cut mono-chromator was used [16].

Lanthanum oxide (Reacton, purity 99.999%) after treatment in flow of high purity CO_2 at 773 K for 5 h was characterized by using X-ray diffraction (XRD) technique. XRD experiment was performed using a Siemens D5000 diffractometer with the CuKα radiation under standard acquisition conditions. Continuous scans in the range of 2θ from 10° to 80° were used. PCPDFWIN standard spectra software was used to determine the lanthanum dioxycarbonate phase.

3. Results and discussion

Figure 2(a) shows a comparison of formation rates of benzene over 1, 2, 3, 6 and 10% Mo/H-ZSM5 catalysts prepared by CVD method and that catalyzed over 10% Mo/H-ZSM5 prepared from physical mixture (denoted as a 10% Mo(PM)). We can see that catalysts with low loading of Mo show relatively high and stable formation rate of benzene while catalysts with 6 and 10% Mo loading give very low formation rate of benzene. In contrast, 10% Mo(PM) catalyst presents similar formation rate of benzene to the 1% Mo prepared by CVD after 400 min in methane stream but with stronger tendency of deactivation for benzene formation. It appears that the catalytic activity differs significantly according to preparation method. The difference may result from an excess of MoO_3 over full coverage of support surface. The excess of MoO_3 sublime out to the atmosphere and the catalyst with good catalytic performances is obtained as in the case of 10% Mo(PM) when the catalyst was calcined in air. The excess of MoO_3 in CVD preparation, on the other hand, has nowhere to sublime but forms inactive $Al_2(MoO_4)_3$ [7] *via* reaction with Al framework or plugs the micropores of H-ZSM5 support, which are essential for the reaction. In other words, zeolite catalyst with large particle size of Mo species on the outer surface and with partly or completely blocked channels by Mo species can work like an unsupported Mo catalyst producing large amount of coke and ethylene as we observed for catalysts with high loading of Mo in H-ZSM5. The effect of the molybdenum loading on the catalytic performance of Mo/H-ZSM5 catalysts is shown in figure 2(b). It is evident that

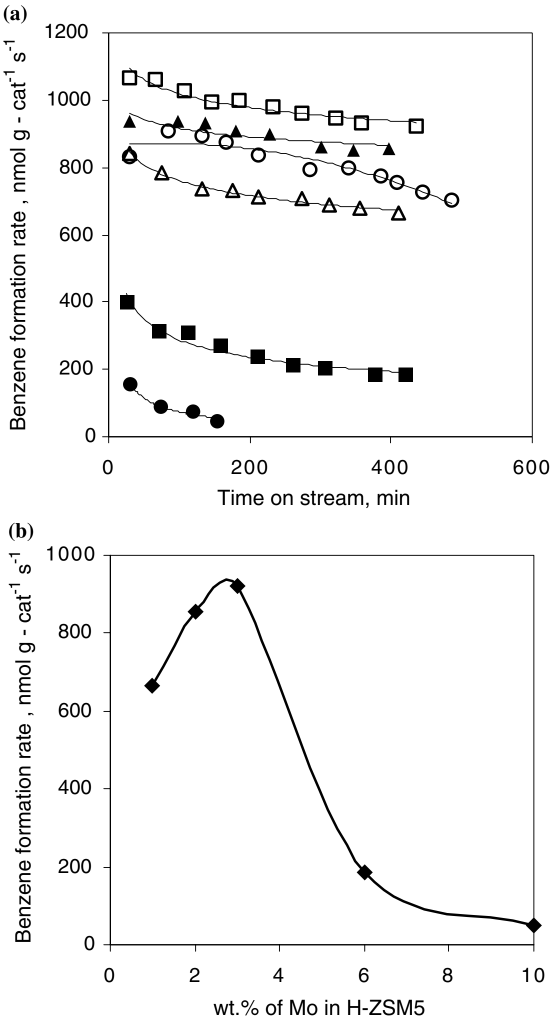

Figure 2. (a) Formation rates of benzene on catalysts prepared by CVD- 1% Mo (△), 2% Mo (▲), 3% Mo (□), 6% Mo (■), 10% Mo (●) and 10 % Mo/PM (○) at reaction conditions: 998 K, 3 × 10^5 Pa and 2500 mL g^{-1} h^{-1} of methane with 2% CO$_2$; (b) Changes in the formation rate of benzene as a function of the loading amount of Mo in Mo/H-ZSM5 catalysts.

Table 1
Catalytic performance on Mo/H-ZSM5 in methane dehydrocondensation for catalysts prepared by CVD in fused ampoule (Static mode)[a]

Catalysts wt%	Time (h)	Conversion[b] (%)	Selectivity for product (%)[c]				
			C$_2$	Bz	Tol	Naph	Coke
1%Mo	6	5.3	11	67	5	6	11
2%Mo	6	6.4	7	64	4	6	19
2%Mo[d]	6	5.3	10	68	5	6	11
3%Mo	6	6.3	5	74	5	8	8
3%Mo[e]	6	6.9	5	54	3	14	24
6%Mo	3	3.5	26	47	6	7	14
10%Mo	3	5.0	12	6	1	0	81
3%Mo–0.5La	7	5.5	10	75	5	6	4
4.3%Mo [7][f]	–	1.7	17	27	–	4	52

[a] The catalytic reaction was conducted at 998 K, 3 × 10^5 Pa, and SV = 2500 mL/h/g with 2% CO$_2$ in methane feed.

[b] Methane conversion.

[c] Selectivity for product excluding CO$_x$; C$_2$ = ethane + ethylene, Bz = benzene, Tol = toluene, Naph = naphthalene.

[d] Catalyst heated at 773 K for 60 h.

[e] Catalyst prepared by physical mixing.

[f] Catalyst prepared by CVD using flowing system. Reaction conditions: 950 K, GHSV = 750 h^{-1}, 1 atm.

optimal loading of Mo in H-ZSM5 is in the range of 2–3%. 2% Mo catalyst was heated for 5 and 60 h and no large difference was noticed in catalytic performance of both catalysts (table 1). It seems that time is not crucial factor in preparation of molybdenum catalyst in above method. Maximum activity of benzene formation on Mo/H-ZSM5 with ca. 3 wt% of Mo may suggest optimal content of the MoO$_3$ in H-ZSM5 and near its monolayer dispersion capacity. Russel and Stokes [17] reported that a maximum dehydrogenation activity of MoO$_3$/Al$_2$O$_3$ catalyst occurred when the Al$_2$O$_3$ surface was covered completely by a monolayer of Mo-oxide. Rondon *et al.* [18] suggested that surface coverage of a catalyst by the active component can be an index of catalytic activity. Borry *et al.* [7] proposed an exchange stoichiometry of MoO$_x$ species with H$^+$ for about one Mo per 1.24 H. In our case for H-ZSM5 with SiO$_2$/Al$_2$O$_3$ = 40, the MoO$_3$ content would be ca. 2.4 wt% if all the MoO$_3$ remained in the exchanged sample after treatment in vacuum. The same authors claim that Mo/H-ZSM5 catalyst prepared by physical mixing with less Mo than that required to form a single MoO$_3$ layer (1–2 wt% Mo) do not lose Mo by sublimation after heating at 773 K in air. Mestl and Knözinger [19] proposed similar opinion that MoO$_3$ are immobile after anchor on AlO$_x$ sites. Thus, these assumptions and kinetic results may suggest an effective spreading of MoO$_3$ in 3% Mo/H-ZSM5 as a monolayer. Catalysts performance of 3% Mo/H-ZSM5 distinguishing preparation method either novel CVD or physical mixing is shown in table 1. As we could see, former catalyst shown 20% higher benzene selectivity as well as three times lower coke formation.

TPO profiles of used CVD-Mo/H-ZSM5 catalysts are shown in figure 3. 1% Mo/H-ZSM5 "a" shows shifted CO$_2$ peak towards high temperature (850 K), which was attributed to carbonaceous deposits on the Brønsted acid sites of the zeolite [4,5]. Possibly, the reason for this phenomenon is the low loading of Mo in H-ZSM5. Since highly active 3% Mo catalyst "b" undergoes the lowest carbonization in the reaction among tested catalysts, it may suggest very good distribution of MoO$_3$ on the surface of zeolite. In contrast, overloaded 6% "c" and 10% Mo/H-ZSM5 "d" catalysts appear to be highly carbonized and show shifted peaks CO$_2$ towards lower temperature (810 K). Probably, the carbon in these catalysts is associated with molybdenum as it was reported previously [4]. Kinetic experiments for

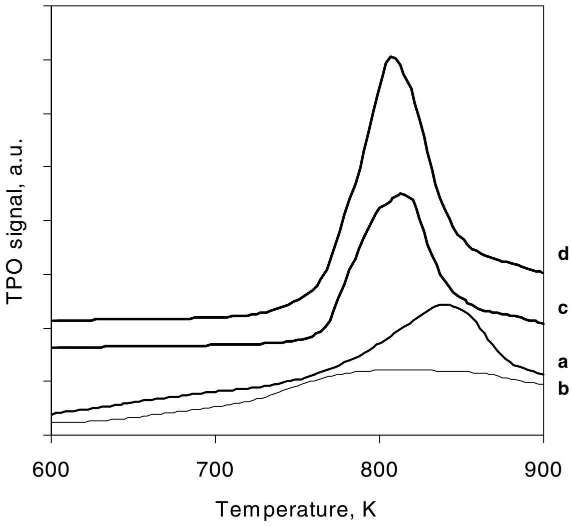

Figure 3. TPO profiles of used Mo/H-ZSM5 catalysts prepared by CVD (a –1%Mo, b – 3%Mo, c – 6%Mo and d – 10% Mo) after 6 h in methane stream with 2% CO_2 at 998 K, 3×10^5 Pa and 2500 mL g^{-1} h^{-1}. TPO experiments were carried out using 30 mg of catalyst at a 10% O_2/He flow rate of 15 mL min^{-1} and temperature raising rate of 10 K min^{-1}.

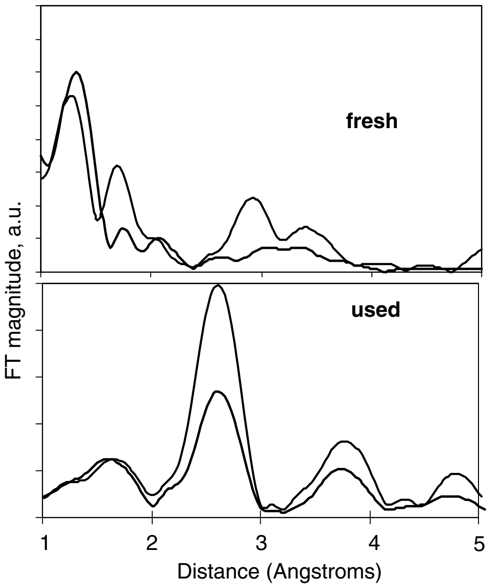

Figure 4. Mo K-edge XAFS Fourier transforms spectra of 3% Mo (thick line) and 6% Mo/H-ZSM5 (thin line) after CVD preparation (fresh) and 3 h in methane stream with addition of 2% CO_2 at 998 K, 3×10^5 Pa and 2500 mL g^{-1} h^{-1} (used).

Table 2
EXAFS Parameters for the 3- and 6-wt% Mo/H-ZSM5 after the reaction with methane (3 atm) at 998 K for 3 h, in comparison with those of Mo foil and Mo

Samples	Mo–Mo		
	C.N.	*R* (Å)	DW[a]
3 wt% Mo/H-ZSM5 CVD	4.3	2.98	0.087
6 wt% Mo/H-ZSM-5 CVD	7.0	2.98	0.082
Mo_2C powder	12	2.97	0.071

[a] Debye–Waller factor.

catalysts described above are summarized in table 1. Selectivity to benzene is higher than 70% for 3% Mo/H-ZSM and that doped with 0.5 wt% La. Selectivity to coke for these catalysts is the lowest and amounted respectively, 8 and 4%. Coke selectivity for the rest of catalysts is well correlated with TPO experiments. Table 1 shows also the result from literature [7] where catalyst 4.3% Mo/H-ZSM5 was prepared in flowing CVD system. Although reaction conditions and Si/Al ratio were different from ours, we could suppose that CVD in static mode gives more active Mo/H-ZSM5 catalyst than that synthesized in flowing CVD system. The effect of addition of La to Mo/H-ZSM5 will be discussed in the latter part of this report.

Figure 4 represents some Fourier transform functions of 3% Mo and 6% Mo/H-ZSM5 catalysts prepared by CVD method. 3% Mo (fresh) shows practically one major distance for Mo–O at ca. 1.4 Å that might be highly dispersed Mo oxide in the internal channels of zeolite (5.4 × 5.6 Å). In case of 6% Mo (fresh) we observe additional peaks at ca. 1.75 Å and ca. 3 Å. It may suggest non homogeneous distribution of MoO_3 in H-ZSM5. After the reaction with methane (figure 4 used), the Mo oxide species are converted to Mo_2C clusters, which appear as a characteristic peak at 2.7 Å. The structural information abstracted from the curve fitting of the FT function for the samples of 3% and 6% Mo/H-ZSM5 are listed in table 2. After the carbonization with methane at 998 K for 7 h, the Mo oxide species are converted to Mo_2C clusters (Mo–Mo: C.N. = 4.3–7.0, $R = 2.98$ Å) in comparison with those of the Mo_2C reference (Mo–Mo: C.N. = 12, $R = 2.97$ Å). Although the characteristic peak for Mo_2C (2.7 Å, figure 4 used) is two times intensive in case of 6% Mo comparing with 3% Mo, we observe much better catalytic performance for the last one (table 1). As we concluded above, the 6% Mo catalyst may have some excess of Mo_2C clusters on the outer surface of zeolite, and in consequence pore mouth of zeolite can be blocked. Selectivity to ethylene and benzene for this catalyst amounted 26% and 47%, respectively (table 1), thus oligomerization of C_2 products towards benzene was decreased possibly due to steric constraints of pore mouth in zeolite.

Finally we will consider the effect of lanthanum addition to 3% Mo/H-ZSM5 catalyst. We observe considerable decrease in the formation rate of coke on non-optimized 3% Mo–0.5% La/H-ZSM5 system comparing with 3% Mo/H-ZSM5 (figure 5a). It is very interesting that at the same time formation rate of CO was higher on Mo–La/H-ZSM5 comparing with monometallic catalyst (figure 5b). On the other hand bimetallic

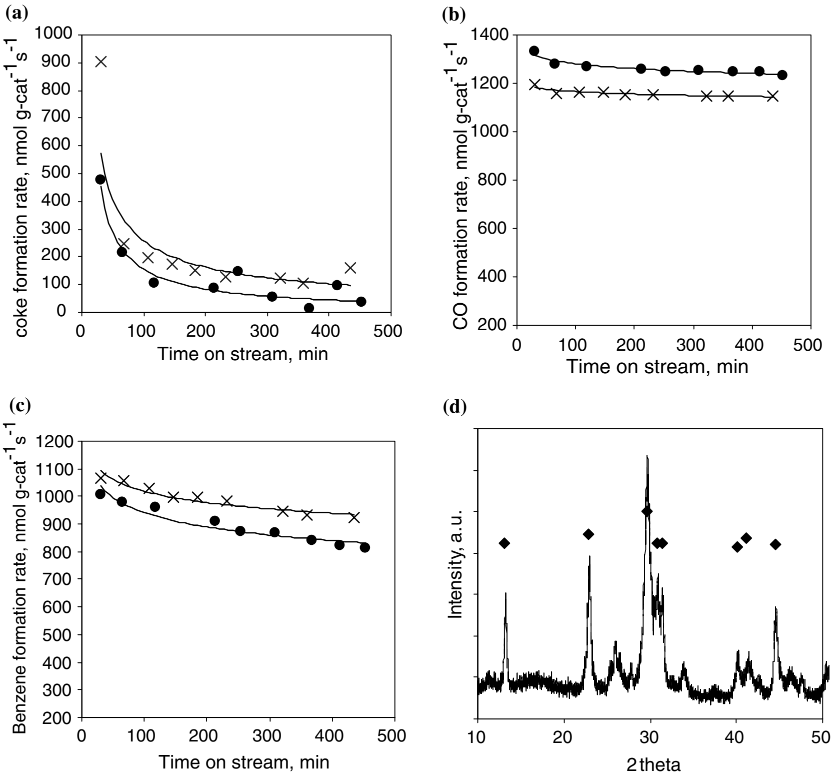

Figure 5. Effect of La_2O_3 addition on the formation rates of (a) Carbon, (b) CO, (c) Benzene on 3 wt% Mo/H-ZSM5 (X) and 3Mo–0.5La wt%/H-ZSM5 (●). Reaction condition: CH_4 with 2% CO_2 at 998 K, 3 ×10^5 Pa and 2500 mL g^{-1} h^{-1}. (d) XRD spectra of lanthanum dioxycarbonate ($La_2O_2CO_3$ Ia) obtained after treatment La_2O_3 with CO_2 at 773 K for 3 h, (◆) reference spectra [21].

catalyst gave a little lower formation rate of benzene than monometallic (figure 5c). It is well known that CO_2 reacts with basic La_2O_3 and produces $La_2O_2CO_3$ species [9,10], according to the following reaction:

$$CO_2 + La_2O_3 \leftrightarrow La_2O_2CO_3 \qquad (1)$$

The authors of refs. [9] and [10] suggest that formation of lanthanum oxycarbonates possibly help to scavenge carbon from support surface or metallic phase, as shown in reaction (2):

$$La_2O_2CO_3 + C^*(\text{carbon deposit}) \rightarrow La_2O_3 + 2CO + * \qquad (2)$$

XRD experiment confirmed that La_2O_3 was almost completely transformed to crystallographic $La_2O_2CO_3$ (type Ia) phase after reaction with CO_2 at 773 K for 5 h (figure 5d). The sum of reactions (1) and (2) gives the well-known Boudouard's process. Kinetic study showed that reaction (1) is a fast step, while reaction (2) is slow in the sequence [20]. Possibly in case of Mo–La/H-ZSM system we are dealing with scavenging surface carbon *via* Boudouard and oxycarbonate decomposition (2) reactions. This may be one of the rational reasons of higher formation rate of CO on Mo–La/H-ZSM5 (figure 5b). These facts could explain also lower formation rate of benzene on Mo–La/H-ZSM5 catalyst as an effect of partial oxidation of Mo_2C active phase (figure 5c). Probably confirmation of the above presented hypothesis required $^{13}CO_2$ isotopic labeling experiment in further investigation. This results indicate that the presence of La_2O_3 on the outer surface of zeolite is beneficial to low coke deposition.

4. Conclusions

In summary, 3% Mo and 3% Mo–0.5% La/H-ZSM synthesized by CVD in static mode exhibited excellent time-on-stream behavior, high aromatic and minimal coke selectivity. Catalyst preparation using CVD method in static mode is relatively simple, effective and easy for scaling-up of the catalytic material. Doping of Mo/H-ZSM5 with small amount of La_2O_3 provides additional way for scavenging surface carbon *via* mechanism similar to Boudouard reaction during methane dehydroaromatization with few percent of CO_2.

Acknowledgments

A.M. thanks the Japan National Fund of Scientific Research for a postdoctoral research fellowship (COE) at Catalysis Research Center, Hokkaido University and Dr. Z. Kaszkur from IPC PAS [b] for a helpful discussion of XRD spectrum.

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