Preparation of Mo_2C/HZSM-5 and its catalytic performance for the conversion of n-butane into aromatics

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Abstract

The preparation of α-MoC_{1-x}/HZSM-5 and β-Mo_2C/HZSM-5 from the carburisation of MoO_3/HZSM-5 by n-C_4H_{10}/H_2 were investigated. It is found that α-MoC_{1-x}/HZSM-5 can be produced from the carburisation of MoO_3/HZSM-5 by n-C_4H_{10}/H_2 between 813 and 973 K. The treatment of α-MoC_{1-x}/HZSM-5 with H_2 above 873 K leads to the production of β-Mo_2C/HZSM-5. The aromatisation of n-C_4H_{10} was investigated using Mo_2C/HZSM-5 as the catalyst. It shows that n-butane is mainly cracked on HZSM-5, while the production of aromatics is significantly promoted when Mo_2C is loaded on HZSM-5. The optimal molybdenum loading is in the range of 3–6 wt.% and α-MoC_{1-x}/HZSM-5 has better aromatisation performance than β-Mo_2C/HZSM-5. On the other hand, when Mo_2C is supported on HZSM-5, the activity and durability of Mo_2C for the aromatisation of n-butane are greatly improved, the acidity of HZSM-5 is also helpful for the aromatisation performance of Mo_2C/HZSM-5. The effect of temperature on the aromatisation of n-butane indicates that the acidity of HZSM-5 plays predominant role in the activation of n-butane at low reaction temperatures while both Mo_2C and HZSM-5 contribute to the aromatisation of n-butane at high reaction temperatures. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: n-C_4H_{10}; Mo/HZSM-5; Molybdenum carbide; Aromatisation

1. Introduction

A considerable amount of light alkanes, such as propane and butane, are not only contained in natural gas but also formed as by-products in petroleum refinery. Aromatisation is one of the ways to upgrade these alkanes. The use of aromatics, in particular benzene, as blending components in gasoline gradually loses its importance because of environmental constraints. But benzene can be transformed to toluene and xylenes by alkylation; moreover, aromatics are important building blocks for the chemical industry. So the research of the aromatisation of lower alkanes are still necessary.

Bifunctional materials with acid sites and dehydrogenation sites are effective catalysts for the aromatisation of lower alkanes [1–6]. ZnO/HZSM-5 and Ga_2O_3/HZSM-5 are the best catalysts for the aromatisation of C_2–C_5 lower alkanes. While Mo_2C/HZSM-5 is efficient to catalyse the aromatisation of CH_4 and C_2H_6 [7–9]. MoO_2 or Mo_2C can catalyse the dehydrogenation of alkanes [10–12], so it is expected that MoO_2/HZSM-5 and Mo_2C/HZSM-5 could be the catalysts for the aromatisation of C_3H_8 and C_4H_{10}. In fact, the aromatisation of C_3H_8 over Mo_2C/HZSM-5

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was reported recently [13] and C_4H_{10} could also be aromatised over Mo/HZSM-5 [14]. Our previous work disclosed that Mo_2C/HZSM-5 has better catalytic performance than MoO_2/HZSM-5 for the aromatisation of n-C_4H_{10} [15]. In this work, the aromatisation of C_4H_{10} over Mo_2C/HZSM-5 is further investigated to understand the roles of Mo_2C and HZSM-5 played in the aromatisation of n-butane.

Fcc α-MoC_{1-x} and hcp β-Mo_2C are often used as catalysts [10–12,16–21]. Hcp β-Mo_2C is usually prepared from the carburisation of MoO_3 by CH_4/H_2 using TPR method. Fcc α-MoC_{1-x} can be prepared from the carbursation of MoO_xC_y (or γ-Mo_2N) by CH_4/H_2, or the carburisation of MoO_3 containing noble metals by CH_4/H_2. But for the aromatisation of n-C_4H_{10}, the procedure from MoO_3 to α-MoC_{1-x} through MoO_xC_y (or γ-Mo_2N) is complicated and noble metals added to Mo_2C/HZSM-5 can be a contaminant. So alternative method should be employed to prepare α-MoC_{1-x}/HZSM-5 for the present case.

MoO_3 can be carburised by C_4H_{10} to α-MoC_{1-x} and β-Mo_2C at different temperature ranges [15,22,23], while the interaction between the support and the molybdenum species might lead to the failure to prepare α-MoC_{1-x}/HZSM-5 in some cases [22]. So the preparation of α-MoC_{1-x} or β-Mo_2C/HZSM-5 from the carburisation of MoO_3/HZSM-5 by C_4H_{10} was investigated before the study of the aromatisation of C_4H_{10} over Mo_2C/HZSM-5.

2. Experimental

The precursor, MoO_3/HZSM-5, was prepared by the incipient impregnation of HZSM-5 ($SiO_2/Al_2O_3 = 30, 80$) with aqueous solution of ammonia *para*-molybdenate at room temperature for 24 h followed by a drying at 393 K for 12 h and a calcination in air at 773 K for 6 h. The catalyst sample was pressed into granules with the size of 425–600 μm for the catalytic test.

Fcc α-MoC_{1-x}/HZSM-5 was prepared from the carburisation of MoO_3/HZSM-5 by C_4H_{10}/H_2. In detail, MoO_3/HZSM-5 was firstly treated by 10% (v/v) n-C_4H_{10}/H_2 with a flow rate of 50 ml/min for 15 min at 673 K, then continuously at 873 K (or at 833 K) for 1 h, and/or at 898 K for 1 h, and/or at 923 K for 0.5 h, and/or 973 K for 1 h. The ramp rate between the temperatures was 6 K/min.

Hcp β-Mo_2C/HZSM-5 was prepared from the carburisation of MoO_3/HZSM-5 by CH_4/H_2. MoO_3/HZSM-5 was treated by 10% (v/v) CH_4/H_2 with a flow rate of 50 ml/min between 673 and 903 K at a ramp of 6 K/min, then at 903, 933, 953 and 973 K for 0.5, 1, 1 and 0.5 h, respectively. This β-Mo_2C/HZSM-5 was described as β-Mo_2C/HZSM-5 (CH_4).

To test the catalytic performance of Mo_2C/HZSM-5, the catalysts were all prepared in situ. Before the reactants were introduced into the reactor, the reaction system was flushed by He for enough time at lower temperature and then the reactor temperature was heated up to and kept at the reaction temperature for 0.5 h.

The catalytic test was undertaken in a fixed bed micro-reactor comprising of a ϕ 13 mm × 3 mm stainless steel tube containing 0.5 g of catalyst. The reactants, 10% (v/v) n-C_4H_{10}/He, flowed with a rate of 7.5 ml/min through the reactor via mass flow controllers (Brooks, Netherlands). C_1–C_5 hydrocarbons were analysed by a Varian 3400 CX GC equipped with a 30 m PLOT-Al_2O_3 column, heavier hydrocarbons were analysed by a Varian 3400 with a 30 m HP-1 capillary column. Six-way valves were used to sample the products. To keep the heavier hydrocarbons as vapour, the gas pipeline between the outlet of the reactor and the sampler on the Varian 3400 was kept above 473 K. H_2 and coke deposit were not analyzed. The conversion of n-C_4H_{10} and the selectivity to the products were expressed by C% and calculated based on the number of hydrocarbons in the effluents analysed by GC. To calculate the carbon balance, the volume of the effluent was measured by a wet gas flow meter. The carbon balances were all higher than 80% when n-butane aromatised over Mo_2C/HZSM-5.

X-ray powder diffraction patterns were recorded on a Siemens D-5005 diffractometer (2θ mode, Cu Kα radiation), step size and scanning rate were set as 0.014° and 0.3 s, respectively.

3. Results and discussion

3.1. Preparation of Mo2C/HZSM-5

3.1.1. Preparation of α-MoC_{1-x}/HZSM-5

Coke deposits are usually produced when Mo_2C is prepared from the carburisation of MoO_3 by

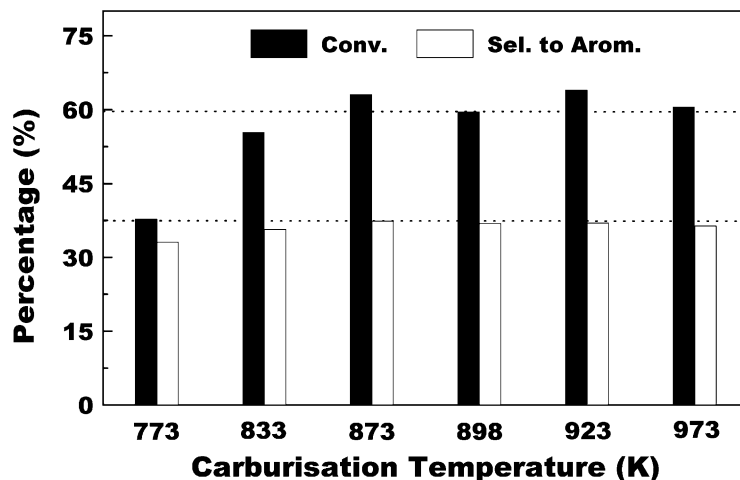Fig. 1. Effect of the final temperature for 15 wt.% Mo/HZSM-5 catalyst ($SiO_2/Al_2O_3 = 80$) carbursied by C_4H_{10}/H_2 on the aromatisation of n-C_4H_{10} at 813 K (the data were taken at 60 min on stream).

C_nH_{2n+2}/H_2 and the coke is often harmful to the catalytic performance of Mo_2C [20,24–27]. So the carburisation temperature was investigated in order to minimize the formation of coke deposits and guarantee the complete carburisation of MoO_3/HZSM-5. The aromatisation of n-C_4H_{10} was chosen as the model reaction to optimize the conditions, the catalyst was characterized by XRD to analyse the phases.

Fig. 1 gives the reaction results when n-butane reacted at 813 K over 15 wt.% Mo/HZSM-5 catalyst carburised by C_4H_{10}/H_2 at different temperature ranges. The selectivities to aromatics for all the catalysts are all in the range of 34–38%. The conversion of n-butane increases from 38 to 60% with the final carburisation temperature rising from 773 to 873 K and keeps stable at ~60% when the final carburisation temperature is in the range of 873–973 K. Furthermore, for the Mo/HZSM-5 catalyst with the final carburisation temperature at 773 K, the conversion of n-butane decreases firstly and then increases with time on stream (which is not shown here). According to the literature [15], this kind of variation in conversion reflects the carburisation of MoO_x, so the reaction results suggest that bulk MoO_x on 15 wt.% Mo/HZSM-5 was not carburised completely by C_4H_{10}/H_2 at 773 K.

Fig. 2 shows the XRD patterns of Mo/HZSM-5 samples after the Mo/HZSM-5, which had been treated by C_4H_{10}/H_2 at different temperatures, catalysed the reaction of n-C_4H_{10} at 813 K. The XRD patterns for all the catalysts treated with n-C_4H_{10}/H_2 are the same, no peaks of MoO_x but two broad peaks with 2θ at 36.8 and 41.2° due to α-MoC_{1-x} are observed. In other words, the XRD results indicate that the bulk
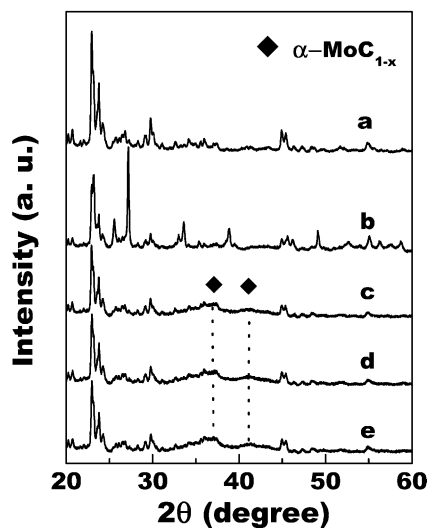

Fig. 2. XRD patterns of: (a) HZSM-5; (b) MoO_3/HZSM-5 (15 wt.% Mo) and 15 wt.% Mo/HZSM-5 samples carburised by C_4H_{10}/H_2 with the final temperature at (c) 773 K; (d) 833 K; (e) 973 K after the reaction of n-C_4H_{10} at 813 K.

MoO_x of 15 wt.% Mo/HZSM-5 are all transformed into α-MoC_{1-x}.

Because the XRD patterns of the catalysts were recorded after the reaction of n-butane at 813 K and MoO_x/HZSM-5 were treated by n-C_4H_{10}/H_2 before the reaction. The Mo/HZSM-5 catalyst, which was not completely carburised by n-C_4H_{10}/H_2 into Mo_2C/HZSM-5 at 773 K, could be further caburised at 813 K by n-butane. Accordingly, the temperature for the carburisation of MoO_x of 15 wt.% MoO_x/HZSM-5 by n-C_4H_{10}/H_2 is between 773 and 813 K.

It is believed that the production of MoO_xC_y/HZSM-5 is important to prepare α-MoC_{1-x}/HZSM-5 from the carburisation of MoO_3/HZSM-5 by n-C_4H_{10}/H_2, so MoO_3/HZSM-5 was usually treated by C_4H_{10}/H_2 at 623 K longer than 24 h to assure the formation of MoO_xC_y [22]. The present results show that the treatment of MoO_3/HZSM-5 at 623 K by C_4H_{10}/H_2 for a long time is unnecessary, α-MoC_{1-x}/HZSM-5 can be produced directly at 813–973 K when C_4H_{10}/H_2 is used as the reactants.

Although the MoO_x of 15 wt.% Mo/HZSM-5 can be carburised into α-MoC_{1-x} by n-C_4H_{10}/H_2 at 813–973 K, the reaction results in Fig. 1 show that the catalyst does not reaches its optimal aromatisation performance until the final carbursation temperature is above 873 K. Moreover, for MoO_3/HZSM-5 with high molybdenum loading [15], the carburisation of MoO_3 below 853 K is slow. All these factors led us

to choose 923 K as the final carburisation temperature for 0–40 wt.% Mo/HZSM-5 samples.

3.1.2. Optimization of Mo_2C/HZSM-5 catalyst

According to the literature, the coke deposits on carbide can be removed by the treatment with H_2 or inert gas [11,12,25–27]. So the freshly prepared α-MoC_{1-x}/HZSM-5 was further treated by H_2 or He flow at different temperature for 1.0 h. The aromatisation reaction of n-butane was still chosen as the model reaction and the bulk phases of the Mo/HZSM-5 catalysts were analysed by XRD.

The analysis of the effluents by GC shows that there were no hydrocarbons when α-MoC_{1-x}/HZSM-5 was treated with He at 873 K or H_2 at 773 K. While CH_4 was detected at 823 K and large amounts of CH_4 was produced at 873 K when α-MoC_{1-x}/HZSM-5 was treated by H_2. So the carbon on α-MoC_{1-x}/HZSM-5 can be partly removed by H_2 above 773 K.

The reaction results when n-butane reacted at 813 K over α-MoC_{1-x}/HZSM-5 treated at different conditions are shown in Fig. 3. The selectivities to aromatics for all the catalysts are $\sim$37%. No difference in the conversion of n-butane is detected between the freshly prepared α-MoC_{1-x}/HZSM-5 and the α-MoC_{1-x}/HZSM-5 treated with He at 873 K. But for the α-MoC_{1-x}/HZSM-5 treated with H_2, the conversion of n-C_4H_{10} decreases from 58 to 48% with the treatment temperature increasing from 773 to
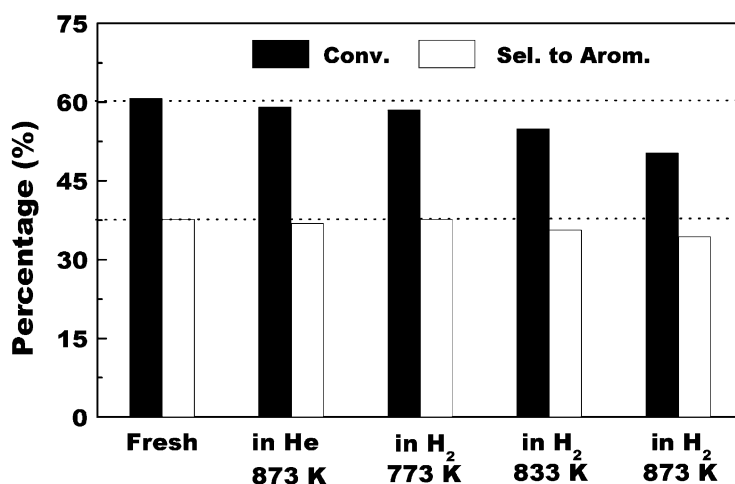

Fig. 3. Aromatisation of n-C_4H_{10} at 813 K over α-MoC_{1-x}/HZSM-5 (20 wt.% Mo, $SiO_2/Al_2O_3 = 80$) pre-treated in various atmospheres (the data were taken at 60 min on stream).
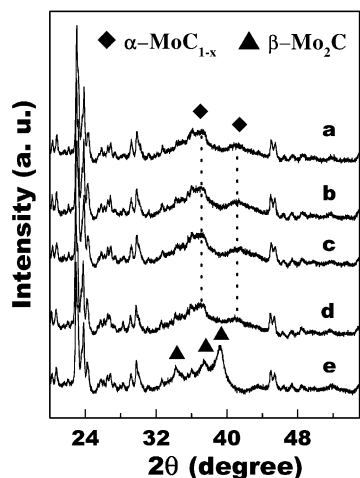
Fig. 4. XRD patterns of: (a) α-MoC$_{1-x}$/HZSM-5 (20 wt.% Mo, SiO$_2$/Al$_2$O$_3$ = 80) without additional treatment, α-MoC$_{1-x}$/HZSM-5 catalysts pre-treated in (b) He at 873 K for 38 min; (c) H$_2$ at 773 K for 60 min; (d) H$_2$ at 823 K for 60 min; (e) H$_2$ at 873 K for 30 min after the reaction of n-C$_4$H$_{10}$ at 813 K.

873 K. So the freshly prepared α-MoC$_{1-x}$/HZSM-5 catalyst without additional treatment exhibits better aromatisation performance than those treated with H$_2$.

Fig. 4 shows the XRD patterns of the α-MoC$_{1-x}$/HZSM-5 catalysts, which had been treated at different conditions, recorded after the reaction of n-butane at 813 K. For the freshly prepared α-MoC$_{1-x}$/HZSM-5 and those treated with He or H$_2$ below 873 K, α-MoC$_{1-x}$ is the sole observed molybdenum phase. But when α-MoC$_{1-x}$/HZSM-5 is treated with H$_2$ at 873 K for 30 min, no α-MoC$_{1-x}$ but β-Mo$_2$C is observed.

The phase change from α-MoC$_{1-x}$ to β-Mo$_2$C in H$_2$ was observed during the H$_2$-TPR of α-MoC$_{1-x}$ [25], but the temperature range for the phase change is not clear. The present result shows that the temperature for the phase change is between 823 and 873 K.

Although α-MoC$_{1-x}$ on HZSM-5 is unstable and changes into β-Mo$_2$C in H$_2$ above 873 K (Fig. 4), it is stable at least below 933 K in n-C$_4$H$_{10}$ [15] and can even endure the high temperature up to 973 K in n-C$_4$H$_{10}$/H$_2$. It is known that the stability of β-Mo$_2$C is better than that of α-MoC$_{1-x}$ in thermodynamics [11,12,28], so the transformation of α-MoC$_{1-x}$ into β-Mo$_2$C in H$_2$ above 873 K is understandable. Nevertheless, the results here show that the atmosphere

has an influence on the stability of α-MoC$_{1-x}$, the existence of n-C$_4$H$_{10}$ in the reactants seems important to stabilize α-MoC$_{1-x}$ on HZSM-5. In fact, the stability of α-MoC$_{1-x}$ on HZSM-5 in hydrocarbons was also observed in the aromatisation of CH$_4$ over α-MoC$_{1-x}$/HZSM-5, α-MoC$_{1-x}$ still kept it structure even after the reaction proceeded at 973 K for 20 h [29].

The results in Figs. 2 and 4 provide us a method to prepare α-MoC$_{1-x}$ and β-Mo$_2$C under similar temperature ranges: MoO$_3$ can be carburised into α-MoC$_{1-x}$ in n-C$_4$H$_{10}$/H$_2$ below 923 K, then α-MoC$_{1-x}$ is further transformed to β-Mo$_2$C in H$_2$ above 873 K. In this paper, β-Mo$_2$C/HZSM-5 prepared in this way was described as β-Mo$_2$C/HZSM-5 (C$_4$H$_{10}$).

Fig. 5 shows the XRD patterns of Mo$_2$C/HZSM-5 prepared by different methods. As indicated by the characteristic peaks at 34.3, 37.3 and 39.4° on the XRD patterns of the Mo$_2$C/HZSM-5 samples prepared from the carburisation of MoO$_3$/HZSM-5 by CH$_4$/H$_2$ (Fig. 5a) or from the treatment of α-MoC$_{1-x}$/HZSM-5 with H$_2$ at 873 K (Fig. 5b), β-Mo$_2$C is the only observed molybdenum phase. The ratio value of $I(39.4^\circ)/I(23^\circ)$ is 0.44 in Fig. 5a while 0.30 in Fig. 5b. The XRD peak at 23° is the strongest peak of HZSM-5 and that at 39.4° is the strongest of β-Mo$_2$C. The higher $I(39.4^\circ)/I(23^\circ)$ ratio value in Fig. 5a means that the crystallinity of the β-Mo$_2$C
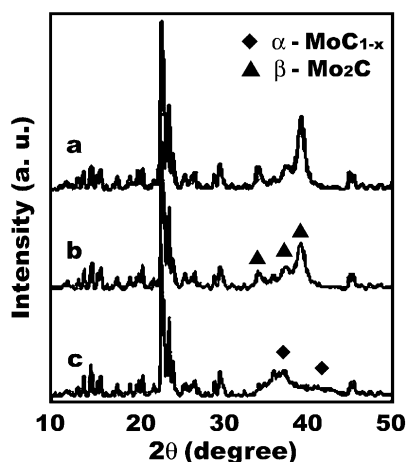

Fig. 5. XRD patterns of the Mo/HZSM-5 (20 wt.% Mo, SiO$_2$/Al$_2$O$_3$ = 80) samples caburised by: (a) CH$_4$/H$_2$; (b) n-C$_4$H$_{10}$/H$_2$ and then treated with H$_2$ at 873 K; (c) n-C$_4$H$_{10}$/H$_2$.
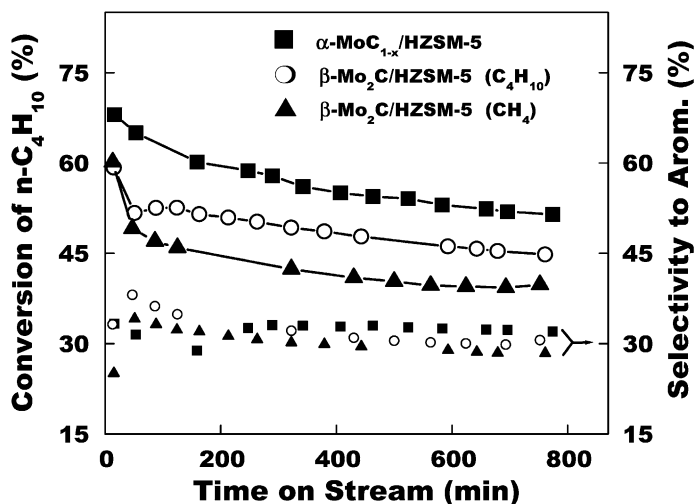
Fig. 6. Aromatisation of n-C_4H_{10} at 813 K over MoC_{1-x}/HZSM-5 (20 wt.% Mo, $SiO_2/Al_2O_3 = 80$) prepared by different methods.

of β-Mo_2C/HZSM-5 (CH_4) is higher than that of β-Mo_2C/HZSM-5 (C_4H_{10}). The molybdenum phase on the Mo/HZSM-5 prepared from the carburisation of MoO_3/HZSM-5 by C_4H_{10}/H_2 is α-MoC_{1-x} as indicated by the two characteristic peaks at 36.9 and ∼41° (Fig. 5c).

Fig. 6 shows the reaction results when n-C_4H_{10} reacted at 813 K over α-MoC_{1-x}/HZSM-5 and β-Mo_2C/HZSM-5 prepared from different methods. The selectivities to aromatics for all the three cases are nearly the same (27–33%) and the conversions decrease with the proceeding of the reaction. But the conversion of n-C_4H_{10} for α-MoC_{1-x}/HZSM-5 is higher than that for β-Mo_2C/HZSM-5, the conversion of n-butane for β-Mo_2C/HZSM-5 (C_4H_{10}) is higher than that for β-Mo_2C/HZSM-5 (CH_4).

As discussed above, the crystallinity of the β-Mo_2C of β-Mo_2C/HZSM-5 (CH_4) is higher than that of the β-Mo_2C/HZSM-5 (C_4H_{10}), the molybdenum loadings on the two catalysts are the same, so the dispersion of the β-Mo_2C of β-Mo_2C/HZSM-5 (CH_4) should be lower than that of the β-Mo_2C of β-Mo_2C/HZSM-5 (C_4H_{10}). Besides that, the final carburisation temperature (973 K) for the β-Mo_2C/HZSM-5 (CH_4) is higher than that (923 K) for the β-Mo_2C/HZSM-5 (C_4H_{10}), this might lead to more coke deposited on the β-Mo_2C/HZSM-5 (CH_4). These two factors could be responsible for the better aromatisation

performance of β-Mo_2C/HZSM-5 (C_4H_{10}) than that of β-Mo_2C/HZSM-5 (CH_4).

When α-MoC_{1-x}/HZSM-5 is treated with H_2 above 823 K, two variations are observed, one is the transformation of α-MoC_{1-x} into β-Mo_2C (Fig. 4), the other is the depletion of the carbon on Mo_2C/HZSM-5 as evidenced by the effluent of CH_4. The depleted carbon could originate from the hydrogenation of protolytic carbon and surface carbidic carbon [25]. Because coke usually leads to the decrease in the activity of the catalyst, the decrease in the activity of Mo_2C/HZSM-5 with the depletion of coke deposits in Fig. 3 suggests that coke deposits on Mo_2C/HZSM-5 is not responsible for the decrease in the aromatisation performance of the Mo_2C/HZSM-5 treated with H_2. Then the decrease in the activity of Mo_2C/HZSM-5 with the depletion of carbon could be attributed to the decomposition of surface Mo_2C, which was suggested by Nagai et al. [30] to explain the decreased activity of Mo_2C with the depletion of coke deposits for the reforming of CH_4 by CO_2 over β-Mo_2C. Apart from that, the dispersion of Mo_2C on HZSM-5 might decrease during the treatment of α-MoC_{1-x}/HZSM-5 with H_2 above 873 K as similar to the cases in Fig. 5 and the intrinsical aromatisation performance of α-MoC_{1-x}/HZSM-5 might be better than that of β-Mo_2C/HZSM-5. All the above three factors could explain the better aromatisation perfor-

mance of α-MoC$_{1-x}$/HZSM-5 than that of β-Mo$_2$C/HZSM-5.

Because α-MoC$_{1-x}$/HZSM-5 shows better performance for the aromatisation of n-butane than β-Mo$_2$C/HZSM-5, the aromatisation of n-butane were investigated using α-MoC$_{1-x}$/HZSM-5 as the catalyst.

3.2. The aromatisation of n-C$_4$H$_{10}$ over α-MoC$_{1-x}$/HZSM-5

3.2.1. Effect of molybdenum loading

The conversion of n-C$_4$H$_{10}$ over α-MoC$_{1-x}$/HZSM-5 with different molybdenum loading at 813 K is shown in Fig. 7. The conversions of n-butane over HZSM-5 and 0.5 wt.% Mo/HZSM-5 are all quite stable, but the conversion decreases from ~80% for HZSM-5 to ~60% for 0.5 wt.% Mo/HZSM-5. When the molybdenum loading of Mo$_2$C/HZSM-5 is higher than 3 wt.%, the conversion of n-butane decreases monotonously with the reaction time and the molybdenum loading. The variation of the selectivity to aromatics is similar to that of the conversion of n-butane, which is not shown here. So the addition of α-MoC$_{1-x}$ into HZSM-5 accelerates the deactivation of the catalyst.

Table 1 shows the distribution of the products during the reaction of n-butane over α-MoC$_{1-x}$/HZSM-5
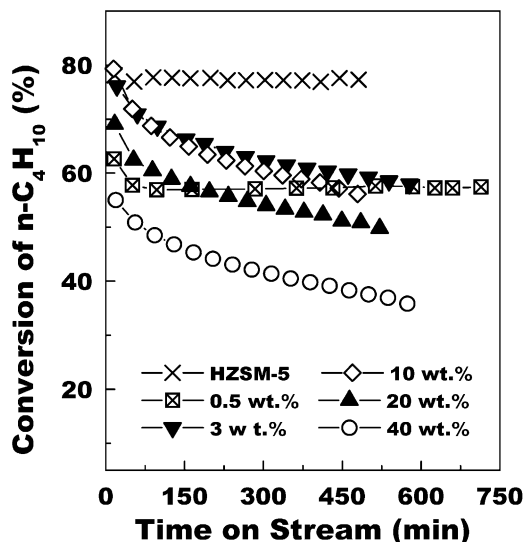

Fig. 7. The conversion of n-C$_4$H$_{10}$ at 813 K over α-MoC$_{1-x}$/HZSM-5 (SiO$_2$/Al$_2$O$_3$ = 80) catalysts with different Mo loading.

at 813 K. The main products for all catalyst samples are CH$_4$, C$_2$, C$_3$ and aromatics. For HZSM-5, the selectivities to C$_2$ and C$_3$ are as high as 37 and 32% (14.4% of C$_3$H$_8$ and 17.5% of C$_3$H$_6$), respectively, the selectivity to aromatics is 13.4%. Benzene (32%) and toluene (47%) are predominated in aromatics, while

Table 1
Effect of Mo loading on the aromatisation of n-C$_4$H$_{10}$ at 813 K over α-MoC$_{1-x}$/HZSM-5 catalyst (SiO$_2$/Al$_2$O$_3$ = 80, the data were taken at 60 min on stream)

Mo (wt.%)	0	0.5	3	10	15	20	40
Conversion (%)	77.5	58.6	70.4	71.3	64.1	61.7	50.1
Yield of aromatics (%)	10.4	9.6	26.8	28.5	23.6	23.2	17.1
Product distribution (%)							
CH$_4$	9.5	10.0	12.3	12.3	11.4	10.0	10.1
C$_2$H$_6$	17.3	19.3	17.3	16.6	14.5	15.6	11.9
C$_2$H$_4$	20.1	17.6	9.5	8.6	11.0	11.7	11.9
C$_3$H$_8$	14.4	10.7	4.5	4.6	4.6	4.5	3.4
C$_3$H$_6$	17.5	17.0	10.2	9.7	11.5	11.9	14.1
i-C$_4$H$_{10}$	1.2	1.6	1.8	1.7	1.5	1.6	2.1
C$_4$H$_8$	5.7	6.1	5.9	6.0	5.5	7.3	11.9
C$_5$	0.9	0.8	0.4	0.3	0.5	0.5	0.4
Aromatics	13.4	16.4	38.1	40.0	36.0	36.8	34.1
Aromatics distribution (%)							
C$_6$H$_6$	32.1	33.1	39.3	42.2	43.6	39.0	45.2
C$_7$H$_8$	47.0	46.2	38.7	36.9	35.4	38.4	36.3
C$_8$H$_{10}$	18.4	17.6	14.3	14.0	13.6	14.1	13.4
C$_9^+$	2.8	3.1	7.7	6.8	7.5	8.6	5.2

the content of C_9^+ aromatics is only 2.8%. These suggest that the main reaction over HZSM-5 is the cracking of n-C_4H_{10} despite that HZSM-5 catalyse the aromatisation of n-butane. For 0.5 wt.% Mo/HZSM-5, the selectivities to the products are close to those for HZSM-5. So the reaction mechanisms should be similar when n-butane reacts over HZSM-5 and 0.5 wt.% Mo/HZSM-5.

When the molybdenum loading increases to 3 wt.%, the distribution of the products changes a lot. The selectivity to aromatics increases sharply to 38%, while the selectivities to C_2 and C_3 decreases simultaneously to 27 and ~15% (4.5% of C_3H_8 and 10.2% of C_3H_6). For aromatics, the contents of C_7 and C_8 decrease to 39 and 14.3%, while the contents of C_6 and C_9^+ increase to ~40 and 8%, respectively.

HZSM-5 loses some acidic sites with the introduction of Mo oxide onto HZSM-5 for the MoO_3/HZSM-5 calcined above 773 K [31,32]. For the aromatisation of n-C_4H_{10} over HZSM-5, Ga/HZSM-5 or Zn/HZSM-5, the selectivity to C_3H_8 is closely related to the acidity of the catalysts, the stronger and denser acidity favors higher selectivity to C_3H_8 [5]. So the decrease in the selectivity to C_3H_8 for Mo_2C/HZSM-5 with 0–3 wt.% Mo (Table 1) reflects on the decrease in the acidity of the catalyst. That is, the decrease in the acidity is one of the reasons for the decrease in the activity when the molybdenum loading increases from 0 to 0.5 wt.% (Fig. 7 and Table 1).

The sharp increase in the selectivity to aromatics with the rising of the Mo loading from 0.5 to 3 wt.% and above shows the role of Mo_2C in the production of aromatics. Mo_2C promotes not only the production of aromatics as indicated by the high selectivity to aromatics for the Mo_2C/HZSM-5 catalyst with the molybdenum loading higher than 3 wt.%, but promotes the conversion of n-C_4H_{10} (Table 1) as suggested by the increased conversion of n-butane when the molybdenum loading rises from 0.5 to 3–10 wt.%.

As for the Mo/HZSM-5 with molybdenum loading higher than 3 wt.%, there are more heavier hydrocarbon products. This could also be true for the coke deposits on Mo/HZSM-5, i.e., there are much more heavier coke deposits on Mo/HZSM-5 with higher molybdenum loadings than 0 or 0.5 wt.%. This can be responsible for the decreased aromatisation performance of Mo/HZSM-5 with the molybdenum loadings or the reaction time on stream (Fig. 7).

According to the yield of aromatics in Table 1, the molybdenum loading is between 3 and 10 wt.% when the catalyst reaches its optimal aromatisation performance. This range is consistent well with that when CH_4 aromatised over Mo/HZSM-5 [31,32] and with the maximum dispersion value when MoO_3 dispersed on HZSM-5, i.e. 4–6 wt.% Mo [14].

Because the addition of α-MoC_{1-x} to HZSM-5 promotes the aromatisation of n-butane, the conventional dual functional mechanism [4–6], i.e. dehydrogenation takes place over Mo_2C, cyclization and aromatisation reactions proceed on the acid sites of HZSM-5, seems effective for the present case. Unfortunately, aromatisation of n-butane can be catalysed by α-MoC_{1-x} [23]. So there is another possibility, the aromatisation reaction mainly take place on α-MoC_{1-x}, the variation of the aromatisation performance of α-MoC_{1-x}/HZSM-5 with molybdenum loading reflects the change in the dispersion of α-MoC_{1-x} on HZSM-5.

Although α-MoC_{1-x} itself can catalyse the aromatisation of n-butane, the conversion is low (<10%) and the durability of α-MoC_{1-x} is not so good (the conversion decreases by ~30% within 4 h at 823 K) [23]. When α-MoC_{1-x} is loaded on HZSM-5, the durability of α-MoC_{1-x} is greatly improved (Fig. 7), which should be related to the coke resistant ability of HZSM-5 [33].

3.2.2. Effect of SiO_2/Al_2O_3 ratio

The reaction results of the aromatisation of n-butane over α-MoC_{1-x}/HZSM-5 with different SiO_2/Al_2O_3 ratio are shown in Fig. 8. For the same n-butane conversion, the temperature for the α-MoC_{1-x}/HZSM-5 with SiO_2/Al_2O_3 ratio of 30 is at least ~50 K lower than that for the catalyst with SiO_2/Al_2O_3 ratio of 80. Similar results are observed for the selectivity to aromatics. So the catalytic performance of the α-MoC_{1-x}/HZSM-5 catalyst with SiO_2/Al_2O_3 ratio of 30 is much better than that of the catalyst with SiO_2/Al_2O_3 ratio of 80. It is known that there are more strong acidic sites on the HZSM-5 with SiO_2/Al_2O_3 of 30 than on the HZSM-5 with SiO_2/Al_2O_3 of 80 [33,34]. It is obvious that the acidic sites of HZSM-5 promote the aromatisation of n-C_4H_{10} over Mo_2C/HZSM-5 no matter how the aromatisation of n-butane proceeds.
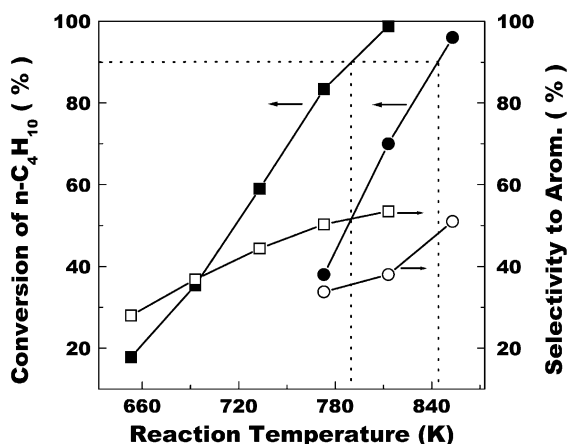
Fig. 8. Effect of SiO$_2$/Al$_2$O$_3$ ratio on the aromatisation of n-C$_4$H$_{10}$ over α-MoC$_{1-x}$/HZSM-5 catalysts (10 wt.% Mo, (■, □) SiO$_2$/Al$_2$O$_3$ = 30, (●, ○) SiO$_2$/Al$_2$O$_3$ = 80, the data were taken at 60 min on stream).

3.2.3. Effect of reaction temperature

The reaction results of the aromatisation of n-butane over α-MoC$_{1-x}$/HZSM-5 (10 wt.% Mo, SiO$_2$/Al$_2$O$_3$ = 30) between 653 and 813 K is shown in Table 2. The conversion is ~18% at 653 K but increases with the rising temperature and n-butane completely transformed at 813 K. The variation of

Table 2
Effect of reaction temperature on the product distribution during the reaction of n-C$_4$H$_{10}$ over α-MoC$_{1-x}$/HZSM-5 (10 wt.% Mo, SiO$_2$/Al$_2$O$_3$ = 30, the data were taken at 60 min on stream)

Temperature (K)	653	693	733	773	813
Conversion (%)	17.5	35.1	56.2	84.5	99.1
Product distribution (%)					
CH$_4$	1.1	2.5	6.0	14.8	27.1
C$_2$H$_6$	8.7	15.1	21.9	22.8	16.1
C$_2$H$_4$	2.4	2.4	2.0	2.5	1.4
C$_3$H$_8$	36.4	26.2	14.8	5.1	1.1
C$_3$H$_6$	6.4	5.8	4.6	2.6	0.4
i-C$_4$H$_{10}$	6.6	3.8	2.2	0.4	0.0
C$_4$H$_8$	4.7	5.4	3.3	1.4	0.1
C$_5$	4.4	1.6	0.2	0.0	0.0
Aromatics	29.2	37.2	45.0	50.4	53.8
Aromatics distribution (%)					
C$_6$H$_6$	11.4	16.2	25.1	39.6	50.8
C$_7$H$_8$	43.9	46.8	43.6	32.6	23.7
C$_8$H$_{10}$	34.0	27.1	19.6	11.8	5.2
C$_9^+$	10.8	9.8	11.6	16.0	20.3

the n-butane conversion with time on stream, which is not shown here, suggests that the reaction is quite stable at 653 K but the deactivation of the catalyst is faster at higher reaction temperatures.

The selectivity to aromatics, ~29% at 653 K, increases to ~50% at 773 or 813 K. The contents of C$_6$H$_6$ and C$_9^+$ aromatics are only 11.4 and 10.8%, respectively, the main aromatics are C$_7$H$_8$ (44%) and C$_8$H$_{10}$ (34%) at 653 K. While at 813 K, the contents of C$_6$H$_6$ and C$_9^+$ increase to 51 and 20%, the contents of C$_7$H$_8$ and C$_8$H$_{10}$ aromatics are only 24 and 5%, respectively. So high temperature is favourable to the production of C$_6$H$_6$ and C$_9^+$ aromatics over the α-MoC$_{1-x}$/HZSM-5 catalyst, which is consistent with the cases in the aromatisation of lower alkanes over Zn (or Ga)/HZSM-5 [4–6]. The selectivities to CH$_4$ and C$_2$H$_6$ are only 1 and 9% at 653 K but increases dramatically to 27 and ~20% at 813 K, respectively. These show the serious cracking of n-butane at high reaction temperatures.

The high selectivity to C$_3$H$_8$ (36.4%) and the relatively low selectivity to aromatics (29%) at 653 K implies that the acidity of HZSM-5 plays a predominating role in the activation of n-butane at lower reaction temperatures. Because the aromatisation performance of HZSM-5 is poor even at 813 K (Table 1), then the increase in the selectivity to aromatics with the reaction temperature suggests that the positive role of Mo$_2$C in the aromatisation of n-butane exert at high temperature. So there is a kinetic or thermodynamic limitation for Mo$_2$C or the dual functions of Mo$_2$C and of HZSM-5 to exert.

4. Conclusions

MoO$_3$/HZSM-5 can be carburised by n-C$_4$H$_{10}$/H$_2$ into α-MoC$_{1-x}$/HZSM-5 between 813 and 973 K, α-MoC$_{1-x}$/HZSM-5 will transform into β-Mo$_2$C/HZSM-5 above 873 K in H$_2$. Based on these results, α-MoC$_{1-x}$/HZSM-5 and β-Mo$_2$C/HZSM-5 can be prepared from the carburisation of MoO$_3$/HZSM-5 by n-C$_4$H$_{10}$/H$_2$ below 923 K.

For the reaction of n-butane on HZSM-5, the selectivity to aromatics is quite low, while the introduction of Mo$_2$C into HZSM-5 greatly promotes the production of aromatics, the durability and activity of α-MoC$_{1-x}$ are improved when it is dispersed

on HZSM-5. Fcc α-MoC$_{1-x}$/HZSM-5 exhibits better catalytic performance for the aromatisation of n-C$_4$H$_{10}$ than β-Mo$_2$C/HZSM-5. For the aromatisation of n-butane over Mo$_2$C/HZSM-5, the acidity of HZSM-5 plays predominant role in the activation and aromatisation of n-butane at lower reaction temperatures, while both Mo$_2$C and HZSM-5 play roles in the production of aromatics at high temperatures.

Acknowledgements

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