Catalysis Letters, Vol. 116, Nos. 3–4, August 2007 (© 2007)
DOI: 10.1007/s10562-007-9102-0

Adsorption properties of methane on Mo and Pd–Ga loaded HZSM-5 at mild temperature

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Received 26 March 2007; accepted 26 March 2007

Methane adsorption on Mo/HZSM-5 and Pd–Ga/HZSM-5 was investigated by TPD. Even at 323 K, methane could adsorb on the catalysts. It dissociated transferred to the high hydrocarbons with temperature increase. The enough concentration of intermediates is necessary step for aromatics formation. The higher ability of hydrogenation over Pd–Ga/HZSM-5 than that over Mo/HZSM-5 was probably the reason for the rich in hydrogenation products and the lack of H_2.

KEY WORDS: methane; TPD; Mo; Pd–Ga; HZSM-5.

1. Introduction

The activation and conversion of methane are two of the most challenging and toughest subjects in catalysis because of the stability of methane molecule. Considerable attention has been paid to the investigation of the methane dehydroaromatization under non-oxidative conditions. The major limitations of this approach are the high price in view of the low conversion of methane as well as the high reaction temperature.

Choudhary et al. [1] found an effective way to convert methane to aromatics at much lower temperature than usual. In the presence of alkenes or higher alkanes over Ga promoted ZSM-5 catalyst, they obtained a higher rate of methane conversion to higher hydrocarbons at 673–873 K. The similar results were reported by the other researchers afterwards [2–10]. The direct formation of benzene from methane at ≤823 K is thermodynamically unfavorable. However, the thermodynamic barrier is reduced as a result of the addition of alkenes or higher alkanes; the value of $\Delta_r G$ becomes negative, depending on the additive, the concentration relative to that of methane, and the reaction temperature.

Most researchers accepted that the break of C–H is the key step in methane dehydroaromatization. The activated methane could be converted into aromatics rapidly through intermediates such as ethylene etc [11,12]. Many experimental results showed that methane could be activated at low temperature. The investigations of the methane adsorption on porous zeolite such as NaA, NaX, NaZSM-5, and Mo/HZSM-5 by FT-IR spectroscopy has been reported [13–17]. Tabata *et al.* [18] concerned on the adsorption state of methane on Ga-ZSM-5 and Cu-ZSM-5. They clarified that methane was adsorbed on Ga-ZSM-5 dissociatively at least at an elevated temperature i.e. 473 K, although it was unknown as to whether methane was dissociated at room temperature. It is well accepted that the break of C–H, formation of intermediates and aromatics at the mild temperature. It is difficult to gain insight into the reaction mechanism because of the lack of experimental data on methane interaction with catalyst surfaces. It is possibly due to the short lifetime of adsorbed methane and reaction intermediates at high temperature. One effective way to clarify the mechanisms of methane activation and aromatics formation is to investigate methane adsorption at mild temperature.

Recently, we have investigated the adsorption of methane on 6%Mo/HZSM-5, 0.5%1%Pd–Ga/HZSM-5, by mass spectroscopy (MS). Direct information about the intermediates of methane transformation over metal-loaded zeolite surface has been obtained. This study is important to an understanding of the methane dehydroaromatization at mild temperature under non-oxidative conditions and also is complementary to our former studies [19–23] on methane conversion with adding of propane over several metal loaded HZSM-5 catalysts under mild conditions.

2. Experimental

Catalysts preparation: 0.5%Pd1%Ga/HZSM-5 was prepared by incipient wetness impregnation of HZSM-5 (SiO_2/Al_2O_3 = 50–75, with an aqueous solution of gallium nitrate. The resulting materials were subsequently dried and calcined in air at 823 K for 6 h. The 0.5%Pd1%Ga/HZSM-5 catalyst was acquired by adding Pd after Ga impregnated it using the same drying and calcining conditions. Similarly, the 6%Mo/

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1011-372X/07/0800–0143/0

HZSM-5 was impregnated with an aqueous solution ammonium of heptamolybdate. The samples were crushed and sieved to 20–40 mesh for catalytic evaluation.

TPD: Methane temperature programmed desorption (TPD) was carried out in a quartz tube (6 mm i.d.) containing 0.2 g catalyst and equipped with a multi-channel MS. The catalyst was first heated under an H_2 stream (30 mL/min) from room temperature to 823 K (10 K/min), and kept at this temperature for 40 min. The catalyst was cooled down in Ar (25 mL/min) to the adsorption temperature and kept for 0.5 h. At the adsorption temperature, the catalyst was exposed with CH4 (30 mL/min) for 0.5 h to make the sample saturated with methane. The catalyst was then cooled down to 323 K in Ar (25 mL/min) and kept for 1 h. The reactor was heated from 323 to 1023 K at 10 K/min under the flow of Ar (25 mL/min) and maintain at 1023 K for 0.5 h. MS intensities for m/e 2(H_2), 15 (CH_4), 28(C_2H_4), 44(C_3H_8) were measured as a function of temperature. m/e 15 was chosen for methane to distinguish it from that of H_2O (18, 17 and 16). All gases were deoxygenated before feeding into line.

Aromatization: The reaction was performed in a continuous-flow micro-reactor made of quartz (6 mm i.d.) with 2 g of the catalyst at atmospheric pressure. The feed was a mixture of 77% methane and 23% nitrogen. The hydrocarbons were analyzed by online gas chromatograph equipped with FID using a PLOT-Al_2O_3/S column.

On propane reaction process, the feed was a mixture of 15% propane and 85% nitrogen. The total GHSV = 410 mL/h·g_{cat}.

Desorption hydrogen: The deactivated catalyst which reacted for 35 min was flushed with Ar (25 mL/min) from 723 to 1173 K, heating rate 5 K/min.

TG: TG profiles were recorded on a PE-TG 7 instrument. The catalyst charge was about 0.02 g, and the flow rate of N_2 and O_2 was 25 mL/min. The catalyst was heated from 298 to 423 K and kept for 20 min in N_2, then was heated from 423 to 1123 K in O_2.

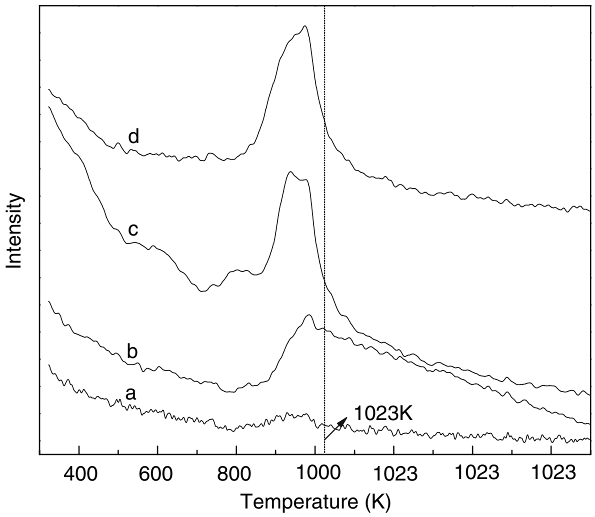

Figure 1. TPD spectra from CH_4 exposed 0.5%Pd1%Ga/HZSM-5, adsorption temperature 323 K, a. CH_4, b. C_2H_4, c. C_3H_8, d H_2.

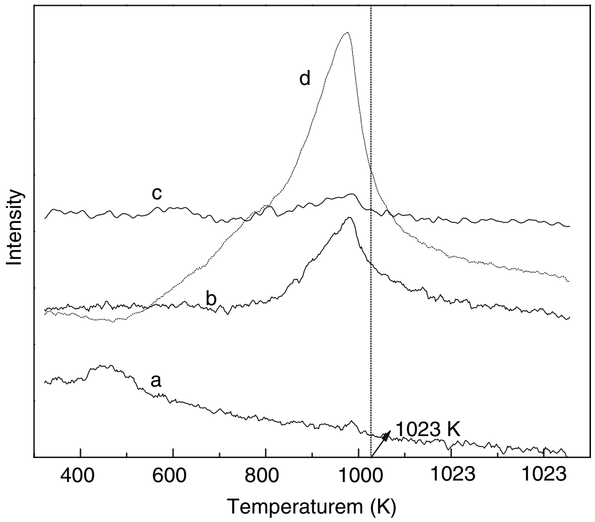

Figure 2. TPD spectra from CH_4 exposed 6%Mo/HZSM-5, adsorption temperature 323 K, a. CH_4, b. C_2H_4, c. C_3H_8, d H_2.

3. Results and discussion

Methane TPD profile on 0.5%Pd1%Ga/HZSM-5 was shown in figure 1. Methane desorbed at around 955 K. The primary products of desorption were H_2, C_2H_4 and C_3H_8 at the same temperature. The methane TPD profile on 6%Mo/HZSM-5 was shown in figure 2. In this case, the methane desorption peak didn't appear and only the primary products were observed. Both figures 1 and 2 demonstrate that methane could be adsorbed on the catalysts even at 323 K. With the temperature ascending, the adsorbed methane was dissociated and transferred to C_2H_6, C_2H_4 and C_3H_8 as suggested by Solymosi [24, 25];

$$2CH_4 \rightarrow 2CH_3^* + H_2$$

$$2CH_3^* \rightarrow C_2H_6 \tag{2}$$

$$2CH_3^* \rightarrow 2CH_2^* + H_2 \tag{3}$$

$$2CH_2^* \rightarrow C_2H_4 \tag{4}$$

$$C_2H_4 + CH_3^* \rightarrow C_3H_7^* \rightarrow C_3H_8 \tag{5}$$

Thus, the intermediates could be formed after the activation of methane at mild temperature. These products are likely the primary products of methane dehydroaromatization and they would oligomerize further to form aromatics as reported by literature [26–29]. Since the thermodynamic barrier could be reduced depending on the additive of alkenes and higher alkanes, and the concentrations relative to that of methane as mentioned above, the formation of aromatics couldn't be observed during the TPD process. The results suggested the concentration of intermediates is too low to form the aromatics at the TPD process. It seems that the enough high concentration of intermediates is also a key step and necessary for aromatics formation at mild temperature besides the C–H break of methane.

Comparing figure 1 and 2, the former appeared more C_3H_8 than later. Almost no CH_4 was detected during the CH_4-TPD. TPD spectra from CH_4 exposed to Mo-HZSM-5 and Pd–Ga/HZSM-5 were shown in figure 3 and 4. When the adsorption temperature raised, the desorption profiles were more or less the same from the two catalysts, except the amount of H_2 desorbed became less and less on the Pd–Ga/HZSM-5. It suggested that the most methane adsorbed as CH_2^* state when exposed in methane at higher temperature. In the TPD process, the two CH_2^* combined to C_2H_4 or oligomerized and hydrogenated to C_3H_8. So there was no excess hydrogen. While on Mo/HZSM-5, the most methane adsorbed as CH_3^* state at different temperature and further dehydrogenate step was taken place in the TPD process. So the hydrogen peak was observed. As figure 5 show that the hydrogen formed in the process of TPD on the Pd–Ga loaded catalyst at 523 K while not formed on Mo loaded catalyst. The hydrogen formation was not detected at 473 K on the Pd–Ga/HZSM-5 might due to the amount of hydrogen was very small. It could be concluded that the methane was adsorbed dissociatively and stronger adsorbed on the Pd–Ga loaded catalyst than Mo at 523 K and above temperature. Note that the hydrogen peak started at 600 K in figure 3, so

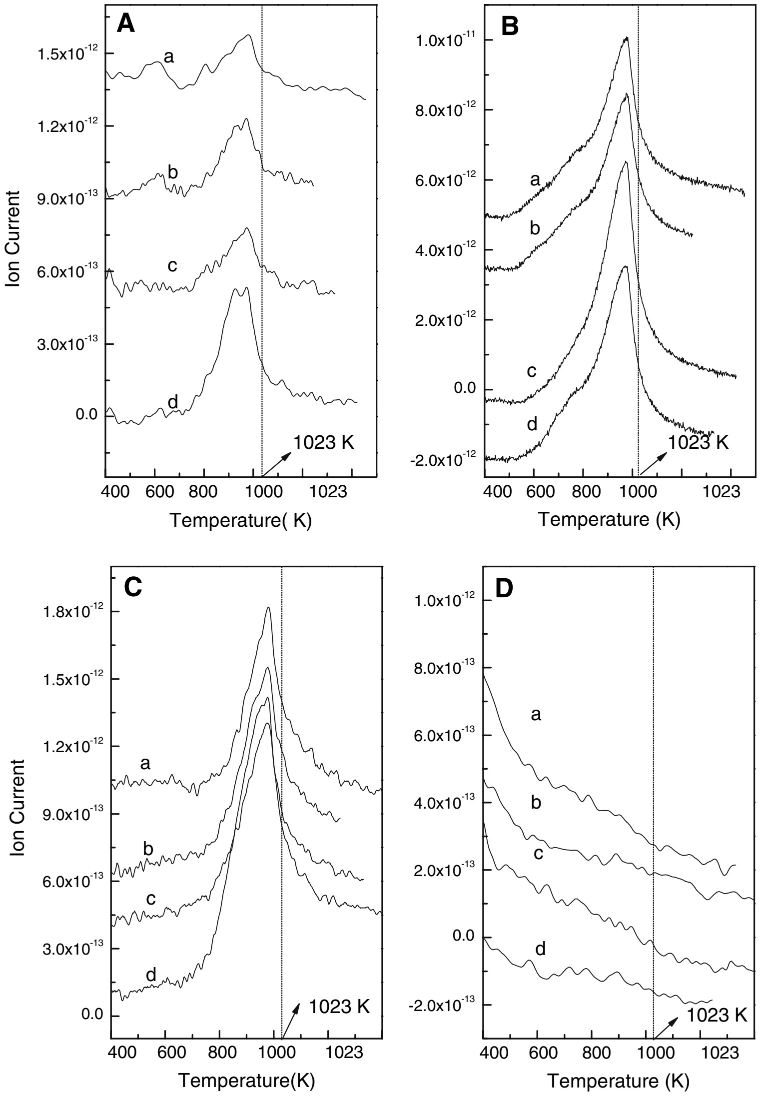

Figure 3. TPD spectra from CH_4 exposed 6%Mo/HZSM-5. The lines were records for (A) C_3H_8; (B) H_2; (C) C_2H_4; (D) CH_4. Adsorption temperature: a. 323 K, b. 473 K, c. 573 K, d. 773 K.

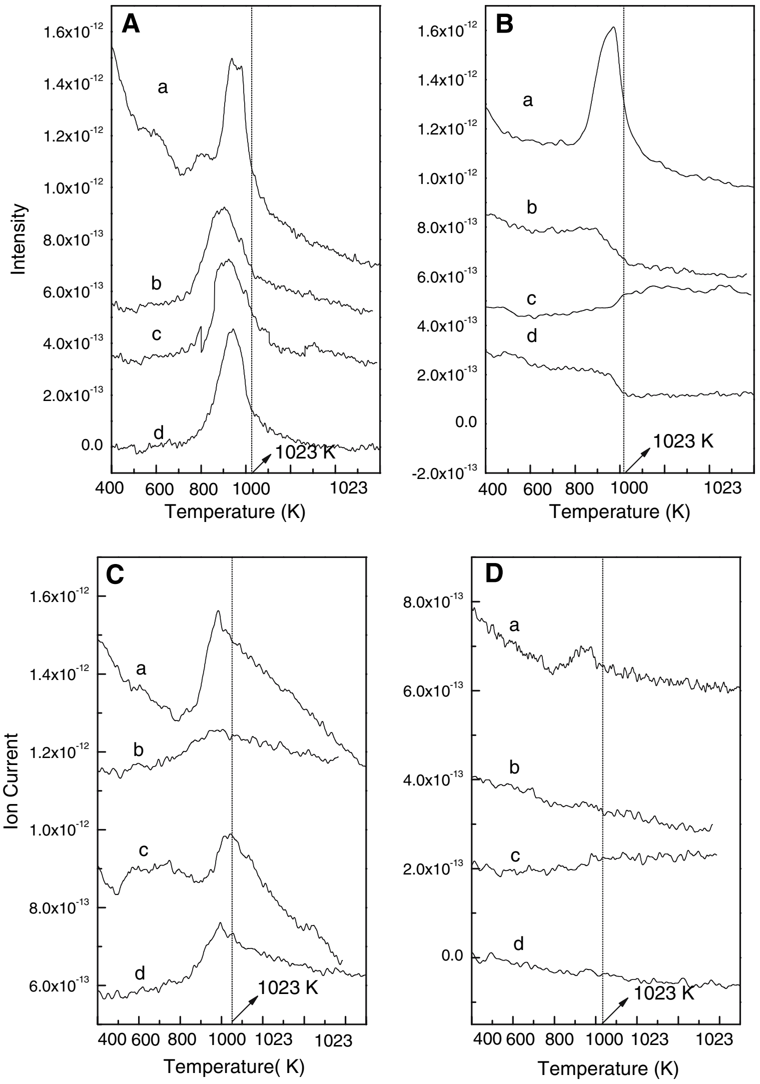

Figure 4. TPD spectra from CH_4 exposed 0.5%Pd1%Ga/HZSM-5. The lines were records for (A) C_3H_8; (B) H_2; (C) C_2H_4; (D) CH_4. Adsorption temperature: a. 323 K, b. 473 K, c. 573 K, d. 773 K.

the methane must be adsorbed dissociatively at 600 K though we didn't clarify which it was adsorbed dissociatively below this temperature on Mo/HZSM-5.

It was found methane could even be transformed into aromatics at 773 and 823 K with accumulation enough intermediates. Transformations of methane over the two catalysts were listed in table 1 and 2. It can be seen that very high selectivity to benzene over Mo/HZSM-5, while quite high selectivity to ethylane and ethylene over Pd–Ga/HZSM-5. Taking the results from CH_4 TPD and aromatization, a general conclusion might be drawn if the processes of CH_4 aromatization be considered roughly as follows:

$$\begin{tikzcd}
CH_4 \arrow[r, "1"] & C_2H_6 \arrow[r, shift left, "2"] \arrow[d, shift right, "5"'] & C_2H_4 \arrow[l, shift left, "3"] \arrow[r, shift left, "7"] & C_6H_6 \arrow[l, shift left, "4"] \\
& C_3H_8 \arrow[u, shift right, "6"'] \arrow[r, shift left, "9"] & C_6H_6 \arrow[l, shift left, "8"] &
\end{tikzcd}$$

Table 1

Effects of time on the transformation of methane over Mo/HZSM-5 catalyst

	Time on stream (min)	Conversion (%)	Selectivity (%)		
			C2	C2=	C6
Methane	240	0.2	16.8	19.8	63.3
	280	0.2	2.9	0	97.1
	310	0.3	0.4	0	99.6

[a] Reaction condition: 823 K, atmospheric pressure, GHSV = 410 ml/h.gcat,CH4/N2 ratio = 10:3.

[b] Data were acquired as referred to the conversion of methane.

[c] Coke was not take into account.

For both catalysts, Step 1 is fast and complete. Almost no CH_4 was detected after adsorbing at 323 K over the catalysts. Step 3, 7, 6 and 8 are more or less related to the hydrogenation. The lack of a desorption

Table 2
Effects of time on the transformation of methane over Pd–Ga/HZSM-5 catalyst

	Time on stream (min)	Conversion (%)	Selectivity (%)		
			C2	C2=	C6
Methane	15	0.3	0	91.8	8.2
	20	0.7	52.1	39.9	7.9
	25	0.4	75.8	.9	18.3
	30	0.1	52.1	0	47.9
	35	0	0	0	0
	[d]20	0.1	100	0	0
	[e]10	0.1	100	0	0

[a] Reaction condition: 773 K, atmospheric pressure, GHSV = 410 mL/h.gcat, CH4/N2 ratio = 10:3.

[b] Data were acquired as referred to the conversion of methane.

[c] Coke was not take into account.

[d] The deactivated catalyst which reacted for 35 min was flushed with Ar from 723 to 1173 K, heating rate 5 K/min, then reacted with methane for 20 min at 773 K.

[e] After step d, flushed with Ar for 30 min at 823 K, then reacted with methane for 10 min at 773 K.

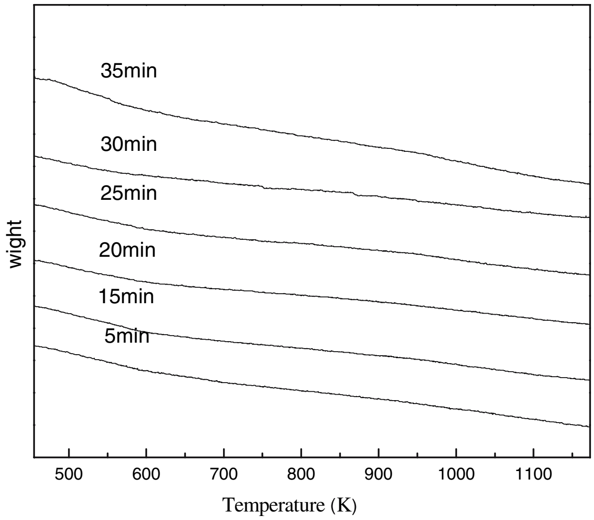

Figure 6. TG curves for deactivated catalysts. In N_2 stream from 293 to 423 K, keep at 423 K for 20 min then in O_2 stream from 423 to 1123 K.

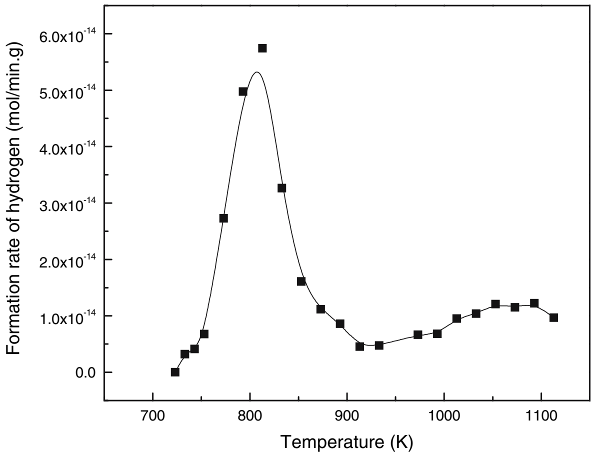

Figure 7. Desorption of hydrogen on the deactivated catalyst with temperature ascending. Flushed with Ar (25 mL/min), heating rate 5 K/min, from 723 to 1113 K. Deactivated catalyst was reacted by methane at 773 K for 35 min.

peak for H_2 and more C_3H_8 in desorption peak is likely attributed to the consumption by hydrogenation reactions of ethylene occurring on Pd besides the strong hydrogen adsorption ability. The Step 1, 2, 4, 5, and 9 depended on further dehydrogenation of C_2H_4 or C_2H_6.

As demonstrated in table 2, the transformation of CH_4 would stop after reaction for 35 min. TG curves (in figure 6) show that the deactivated catalyst deposited a little more coke. Additionally, the hydrogen could desorb with Ar flushed by temperature ascending as figure 7 showed. After the step for hydrogen desorption the deactivated catalyst could transform CH_4 again (see table 2 and figure 8). But the reaction data showed both for 20 min and 10 min on stream, the transformation activity was lower than before and couldn't form the aromatics. It was described to the absorption of hydrogen in Pd and coke suppressed the dehydrogenation of CH_4.

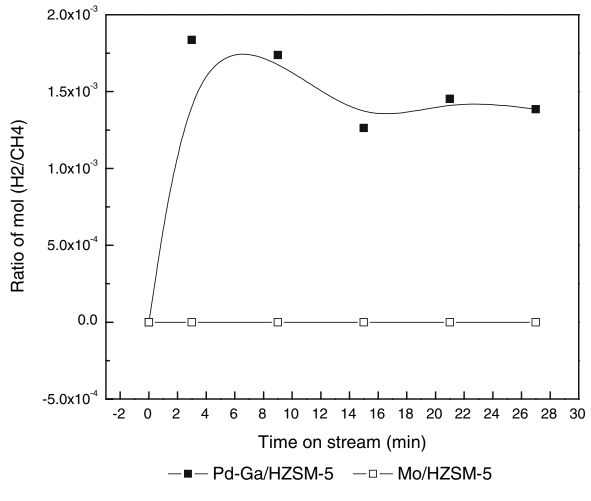

Figure 5. The formation of hydrogen in process of catalysts exposed in CH_4 (25 mL/min). Temperature: 573 K, atmosphere: 1 atm.

Note that even the reaction was carried out at 823 K; the induction period that from methane activity to benzene formation over Mo based catalyst at 823 K was longer than over Pd–Ga/HZSM-5 at 773 K. The tendency for the selectivity to C_2, $C_2 =$ and C_6 are similar. The reasons why there were catalysts have such different behaviors in the induction period need to be further studied.

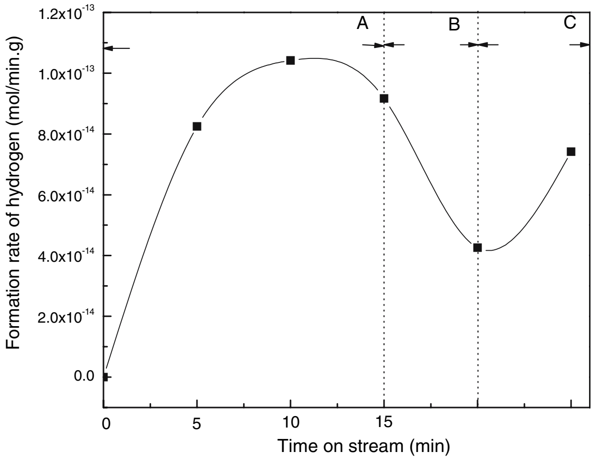

Figure 8. Formation rate of hydrogen over the Pd–Ga catalysts at 773 K. (A) After desorption of hydrogen on the deactivated catalyst then reacted with methane for 15 min. Desorption condition: flushed with Ar (25mL/min), heating rate 5 K/min, from 723 to 1113 K. (B) Desorption hydrogen at 823 K flushed with Ar (25mL/min) for 30 min after step A, then reacted with methane for 20 min. (C) Desorption hydrogen at 823 K flushed with Ar (25 ml/min) for 30 min after step B, then reacted with methane for 10 min.

4. Conclusion

Methane could be adsorbed on Mo and Pd–Ga loaded HZSM-5 catalyst at 323 K and dissociated and transferred to the high hydrocarbons with temperature increase. The enough high concentration of intermediates is needed for aromatics formation. The difference desorption species and reaction products are attribute to the different ability on hydrogenation and dehydrogenation of the catalysts. The rich in hydrogenation products and the lack of H2 during TPD measurement are probably the higher ability of hydrogenation over Pd–Ga/HZSM-5 than that over Mo/HZSM-5.

Acknowledgments

Financial supports from the National Natural Science Foundation of China (No. 20343002, 20433030) and from National Education Ministry are gratefully acknowledged.

References

[1] V.R. Chuddar, A.K. Kin age and T.V. Chuddar, Science 275 (1997) 1286.
[2] J.H. Lunsford, Angrew. Chem. Int. Ed. Engl. 34 (1995) 970.
[3] L. Wang, L. Tao, M. Xie, G. Xu, J. Huang and Y. Xu, Catal. Lett. 21 (1993) 35.
[4] S. Liu, L. Wang, R.O. Nishi and M. Ichikawa, J. Catal. 181 (1999) 175.
[5] O.A. Anunziata, G.A. Eimer and L.B. Pierella, Catal. Lett. 58 (1999) 235.
[6] O.A. Anunziata, G.A. Eimer and L.B. Pierella, Appl. Catal. A 190 (2000) 169.
[7] O.A. Anunziata, G.V. Gonzáez Mercado and L.B. Pierella, Catal. Lett. 87 (2003) 167.
[8] W. Chu and F. Qiu, Top. Catal. 22 (2003) 13.
[9] G.V. Echevsky, E.G. Kodenev, O.V. Kikhtyanin and V.N. Parmon, Appl. Catal. A 258 (2004) 159.
[10] T. Baba, Y. Abe, K. Nomoto, K. Inazu, T. Echizen, A. Ishikawa and K. Murai, J. Phys. Chem. B 109 (2005) 4263.
[11] D. Ma, Y. Shu, M. Cheng, Y. Xu and X. Bao, J. Catal. 194 (2000) 105.
[12] J.A. Labinger and J.E. Bercaw, Nature 417 (2002) 507.
[13] E. Cohen de Lara and Y. Delaval, J. Phys. Chem. 78 (1974) 2180.
[14] E. Cohen de Lara and R. Seloudoux, J. Chem. Soc. Faraday Trans. I 71 (1983) 271.
[15] E. Cohen de Lara, R. Kahn and R. Seloudoux, J. Chem. Phys. 83 (1985) 2646.
[16] T. Yamazaki, Y. Abe, I. Watamuki, T. Ding, S. Ozawa, and Y. Ogino, Chem. Lett. 1457(1987).
[17] L. Chen, L. Lin, Z. Xu, T. Zhang, Q. Xin and P. Ying, J. Catal. 161 (1996) 107.
[18] T. Tabata, M. Kokitsu and O. Okada, Catal. Lett. 25 (1994) 393.
[19] H. Zheng, H. Lou and X. Zheng, Chin. J. Catal. 25 (2004) 255.
[20] H. Zheng, H. Zhu, H. Lou, Z. Hou, J. Fei, Y. Li, H. Xiao, Y. Yang and X. Zheng, Chin. J. Catal. 26 (2005) 49.
[21] H. Zheng, H. Lou, Y. Li, H. Fei, Z. Hou, Y. Xu, S. Wan, S. Wang and X. Zheng, Chem. J. Chin. Univ. 26 (2005) 285.
[22] L. Zheng, D. Xuan, J. Guo, H. Lou and X. Zheng, J. Nat. Gas Chem. 15 (2006) 52.
[23] J. Guo, H. Lou, H. Zhao, L. Zheng and X. Zheng, J. Mol. Catal. A 239 (2005) 222.
[24] F. Solymosi, A. Erdohelyi and A. Szoke, Catal. Lett. 32 (1995) 43.
[25] A. Szoke and F. Solymosi, Appl. Catal. A 142 (1996) 361.
[26] L. Wang, L. Lin, T. Zang and H. Cai, React. Kinet. Catal. Lett. 52 (1994) 107.
[27] O.A. Anunziata, L.B. Pierella, R.G. Marino, React. Kinet. Catal. Lett. 54.
[28] O.A. Anunziata and L.B. Pierella, React. Kinet. Catal. Lett. 55 (1995) 365.
[29] O.A. Anunziata and L.B. Pierella, React. Kinet. Catal. Lett. 55 (1995) 373.