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The effect of ZSM-5 framework in non-oxidative coupling of methane

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Abstract: *We have been studying the effect of acidity of zeolite on its catalytic activity toward non-oxidative coupling (NOC) of CH_4, employing a newly developed catalyst; B-doped MFI-type zeolite (H-[B]ZSM-5). It was prepared by a hydrothermal method with a structural directing agent, TPABr. The 6%Mo/H-ZSM-5 and 6%Mo/H-[B]ZSM-5 catalysts were synthesized by wetness impregnation. The NOC of methane was performed in a fixed bed reactor at 1023 K under atmospheric pressure. The results showed that the CH_4 conversion at TOS of 360 min was around 14% for both catalysts. The 6%Mo/H-[B]ZSM-5 exhibited a higher stability than the other, producing C_2H_4/C_2H_6, C_6H_6 and H_2 at higher yields as well (0.06, 0.11 and 6.49 mol%, respectively) than 6%Mo/H-ZSM-5 (0.04, 0.07 and 4.75 mol%, respectively). Moreover, the coke deposition onto the 6%Mo/H-[B]ZSM-5 was 12.3 %wt. which was lower than 6%Mo/H-ZSM-5 (18.4 %wt.).*

Keywords: Non-oxidative coupling; Methane; Catalyst; H-ZSM-5; Boron; Molybdenum.

1. INTRODUCTION

Due to a fact that methane is the most abundant gaseous hydrocarbon in nature, its catalytic conversion into longer chain hydrocarbons and/or value-added chemicals has attracted researchers in many years. In general, the methane conversion can be performed by several methods such as stream reforming, dry reforming, oxidative coupling (OC) and non-oxidative coupling (NOC) [1]. Among these, according to the long-term benefit, the NOC is considered as the most promising way to utilize methane, and it can serve as a route alternative to OC and the others for producing value-added chemicals with minimized or no CO_2 emission.

In the methane NOC process, methane is converted to higher hydrocarbon products; mainly benzene while together with minor products such as ethylene, ethane and naphthalene, at temperature over 700 K and atmospheric pressure [1-3]. Among combinations of different metallic species (Mo, Zn, W, Fe, and Mn) and zeolites (ZSM-5, ZSM-22 and SAPO-34) that have been studied, Mo/ZSM-5 seems to be the most promising one in terms of the methane conversion [2-3]. It is generally accepted that the Mo/ZSM-5 is a bifunctional catalyst. Mo plays a role of activating C-H bonds of methane inducing the formation of C_2 hydrocarbon species, while the Brønsted acid sites provided by the ZSM-5 control the aromatization of the C_2 species. Most of the previous studies focused on methane NOC to produce benzene, called methane dehydro-aromatization (MDA), as there is increasing demand of aromatic compounds in chemical industry. Another reason is that the benzene production is more favored thermodynamically than that of ethylene [4-5]. However, the methane NOC to ethylene is more interesting because together with C_3/C_4 alkenes it is the most important chemical platform.

Sheng and co-workers [6] recently reported application of a modified ZSM-5 with replacement of boron (B) instead of aluminum (Al) to the methane NOC aiming to decrease the Brønsted acidity. The result showed that the benzene/ethylene selectivities to of 91:5 (methane conversion < 1%), which were much different from those for [Al]ZSM-5 [7], 7:90. Following their achievement, we aimed to synthesize a H-[B]ZSM-5 by employing silica gel as the Si sources instead of fumed silica and improving the synthetic method. We expected that this catalyst would lead to the improvement in the CH_4 conversion and C_2 production. This paper reports performances of the H-[B]ZSM-5 in the methane NOC.

2. MATERIALS AND METHODS

2.1 Catalyst preparation

[B]ZSM-5 was synthesized by a hydrothermal method that is a modification of the method by Sheng and co-workers [6]. Tetrapropylammonium bromide (TPABr), silica gel, and boric acid were used as the template, the silicon and boron sources, respectively. In brief, four chemicals of reagent grades, i.e., 0.44 g of TPABr, 0.08g of NaOH, 0.05g of H_3BO_3, and 0.76g of SiO_2 were dissolved or dispersed in 10ml of deionized water. The resulting suspension was stirred at room temperature until it transformed into a homogeneous gel. Subsequently, the gel was subjected to a Teflon lined stainless steel autoclave (Parr 4745) and crystallized therein at 423 K for 72 h. The crystalline solid was filtered, washed with deionized water until neutralization and then dried at 353 K overnight. The Na-[B]ZSM-5 was prepared after the template removal at 823 K in air for 6h. The Na-[B]ZSM-5 thus prepared was further transformed into NH_4-[B]ZSM-5 by twice repeated ion-exchange in an aqueous solution of NH_4NO_3 at 353 K. The solid was dried in the same way as above. Two types of zeolites in protonated forms were prepared from NH_4-[B]ZSM-5 and NH_4-ZSM-5 (ZEOLYST Int. Inc., CBV 3024E) by calcining them in air at 823 K for 5 h. Those zeolites were denoted by H-[B]ZSM-5 and H-ZSM-5, respectively.

The molybdenum catalysts were prepared by incipient wetness impregnation using ammonium heptamolybdate tetrahydrate (($NH_4)_6Mo_7O_{24} \cdot 4H_2O$) as the molybdenum precursor. The impregnated catalysts were dried at 353

K overnight and then calcined at 823 K under static air for 5 h. The Mo/ZSM-5 catalysts were crushed and sieved to sizes of 212–500 µm prior to the catalytic test.

2.2 Catalytic test

Methane NOC runs were carried out in a fixed bed reactor at 1023 K under atmospheric pressure. The reactor was made of a transparent quartz tube with 8-mm i.d.. A 200 mg of catalyst was diluted by 800 mg of SiC, and then packed into the reactor together with quartz wool plugs. The catalyst was carburized at 1023 K for 180 min while exposed to a continuous flow of CH_4/H_2 mixture (20/80 in vol.) at a rate of 20 ml/min. At the end of the carburization, the gas flow was switched to that of N_2 at 30 ml/min to completely remove the residual CH_4 and H_2. Every methane NOC run was performed by employing a reactant gas consisting of atmospheric CH_4 (50 vol%) and N_2 that was used as not only the diluent but also the internal standard for the product gas analysis. The gas flow rate was fixed at 15 ml/min while the catalyst temperature was maintained at 1023 K. The product gases as well as unconverted methane were analyzed intermittently with a gas chromatograph (GC; Agilent micro GC 490) that was equipped with PoraPLOT Q and Molsieve 5A columns. The methane conversion and selectivity to carbon-containing products were determined on a carbon basis.

2.3 Catalyst Characterization

The X-ray diffractograms (XRDs) of fresh and spent catalysts were recorded on a Rigaku TTR-III diffractometer that employed Cu Kα radiation (50kV, 300mA) at a scanning rate of 0.02 over a 2θ range of 5–50°. Crystalline phases were identified by referring to International Centre for Diffraction Data. The catalyst surface morphology was investigated by scanning electron microscopy (SEM) on a microscope (KEYENCE, VE9800). Catalysts were also subjected to N_2 adsorption/desorption at 77 K on a BELSORP-mini II analyzer for measuring the BET surface area (S_{BET}) and micropore volume. The amounts of coke on spent catalysts were determined by thermogravimetric analysis (TGA) on a Hitachi STA-7200 thermal analyzer). A 10 mg of spent catalyst was heated in air up to 1123 K at a heating rate of 10 K/min while the coke was burned off.

3. RESULTS AND DISCUSSION
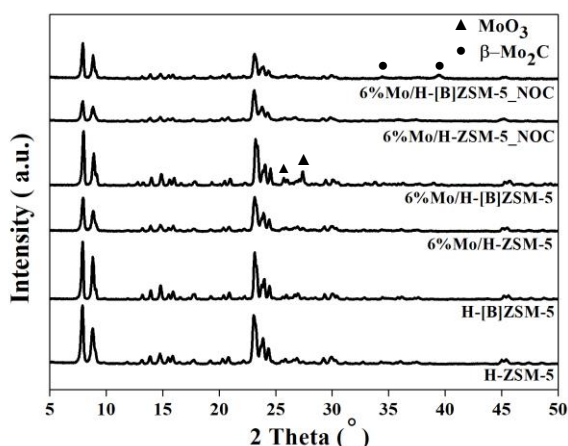
3.1 Catalyst Characterization

Fig. 1. The XRD pattern of all samples.

Fig. 1 displays XRDs of the catalysts. The H-[B]ZSM-5 shows peaks that are assigned well to itself while no diffraction due to amorphous phases. It is also seen for the H-ZSM-5 that the diffraction pattern agrees with that arisen from a typical MFI structure of zeolite (H-ZSM-5, IDDP file number 00-037-0359). The textural properties of the catalysts are listed in Table 1. The H-[B]ZSM-5 has a slightly smaller S_{BET} while a slightly greater micropore volume than the H-ZSM-5. Typical morphologies of the catalysts are given in Fig. 2. The image of H-ZSM-5 (*Photo b*) provides no details of its surface morphology, unfortunately due to aggregation of small particles. The H-[B]ZSM-5 seems to consists of primary particles the sizes of that are well regulated around 20 µm while forming agglomerates.

Table 1. S_{BET} and V_{micro} of fresh and spent catalysts. The spent catalysts are indicated by '_NOC'.

Sample	S_{BET} (m²/g)	V_{micro} (cm³/g)
H-ZSM-5	378.11	0.104
H-[B]ZSM-5	342.72	0.126
6%Mo/H-ZSM-5	348.57	0.092
6%Mo/H-[B]ZSM-5	307.88	0.106
6%Mo/H-ZSM-5_NOC	41.83	0.006
6%Mo/H-[B]ZSM-5_NOC	96.95	0.035

The 6%-Mo impregnation to the H-ZSM-5 causes no change in the XRD pattern but giving smaller diffraction peaks. The 6%-Mo impregnation also arises peaks at 25.73° and 27.42° in the XRD of H-[B]ZSM-5. These peaks occur with a phase of orthorhombic MoO_3 crystals (IDDP file number 00-001-0706). On the other hand, no such peaks are seen in the XRD of the 6%Mo/H-ZSM-5. This indicates high dispersion of molybdenum. The comparison between the SEM images (a) and (c) (see Fig. 2) suggests molybdenum deposition onto the H-[B]ZSM-5, which resulted in decrease in the intensity of the MFI peaks (Fig. 1) and also that in the S_{BET}. Thus, the 6%Mo impregnation decreased S_{BET}'s and V_{micro}'s of the H-[B]ZSM-5 smaller by 7.8% and 11.5%, respectively, and also those of H-[B]ZSM-5 by 10.2% and 15.9%, respectively. This result suggests that molybdenum was deposited onto the external surface of the zeolites and also in micropores.
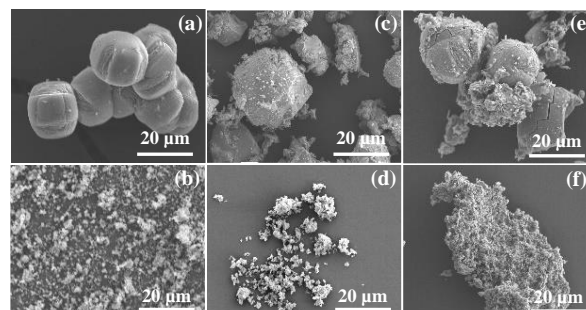

Fig. 2. SEM images of (a) H-[B]ZSM-5, (b) H-ZSM-5, (c) 6%Mo/ H-[B]ZSM-5, (d) 6%Mo/ H-ZSM-5, (e) 6%Mo/ H-[B]ZSM-5_NOC and (f) 6%Mo/ H-ZSM-5_NOC.

Spent 6Mo/H-ZSM-5 and 6Mo/H-[B]ZSM-5 from methane NOC at 1073 K and for 360 min were analyzed by XRD. It was then confirmed that both catalysts main-

tained their MFI structures, but diffraction peaks had lost their initial intensities (see Fig. 1) substantially. This was consistent with macroscopic structural changes of those catalysts. As shown by the SEM image (e), 6Mo/H-[B]ZSM-5 particles seemed to have experienced disintegration in the methane NOC. The XRD, S_{BET} and V_{micro} of the spent catalyst also showed that the particles had suffered from coke deposition. It is seen in Fig. 1 that the spent 6Mo/H-[B]ZSM-5 has small diffraction peaks at 34.53° and 39.58°. These are both attributed to β-molybdenum carbide (β-Mo_2C, IDDP file number 03-065-8766). It was believed that this carbide had occurred from the MoO_3 and played a catalytic role in the methane NOC [2,4].

3.2 Results of catalytic tests

The catalytic performance in the methane NOC was investigated at 1023 K with the following conditions: the space velocity; 4500 ml g^{-1} h^{-1}, pressure; atmospheric, TOS; 360 min.
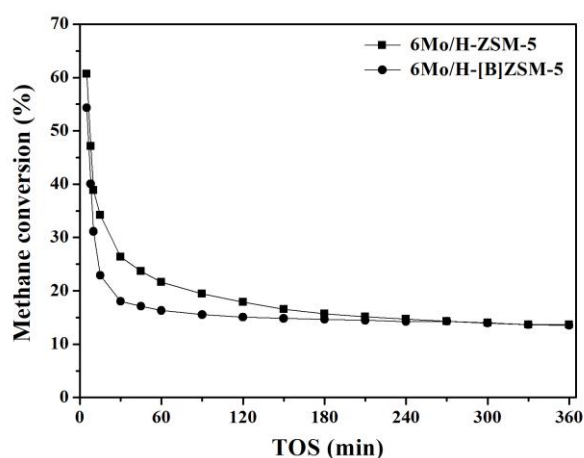
Fig. 3. Methane conversion as a function of time on stream.

Fig. 3 illustrates the methane conversions over 6Mo/H-ZSM-5 and 6Mo/H-[B]-ZSM-5 as a function of TOS. It is seen that both catalysts exhibit the same trends of the methane conversion. The methane conversions for the 6%Mo/H-ZSM-5 and 6%Mo/H-[B]ZSM-5 are initially 61% and 54%, respectively, but afterward decrease steeply to *ca.* 14% probably due to deactivation induced by the coke deposition [8].
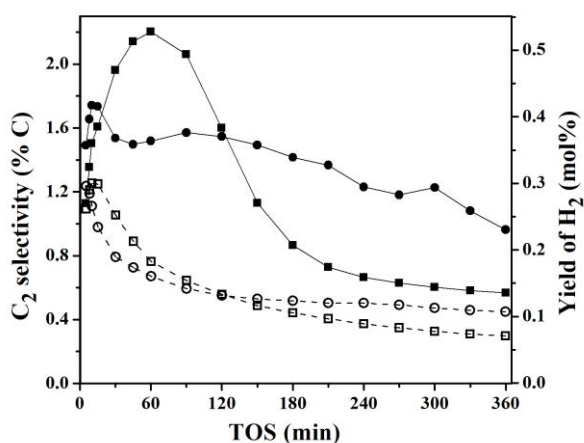
Fig. 4. Changes in C_2 selectivity (closed symbols with solid lines) and H_2 yield (opened symbols with dashed lines) with TOS for 6%Mo/H-ZSM-5 (squares) and 6%Mo/H-[B]ZSM-5 (circles).

Fig. 4 combinedly shows the selectivity to C_2 (C_2H_4 and C_2H_6) and H_2 yield as functions of TOS. The 6%Mo/H-ZSM-5 and 6%Mo/H-[B]ZSM-5 have different C_2 selectivities. The selectivity for the 6Mo/H-ZSM-5 changes through a maximum (ca. 2.2%) around 60 min, and also approaches 0.5–0.6 % later. On the other hand, the selectivity for the 6Mo/H-[B]-ZSM-5 decreases monotonously and slowly. Then, the latter shows a higher selectivity at the end of the run (1.0% *vs* 0.6%). The two catalysts are similar to each other in terms of the H_2 yield and its time-dependent change. The continuous reduction of the yield is an indication of continuous loss of activities. It is noted at TOS ≥ 180 min that the H_2 generation from the 6%Mo/H-[B]ZSM-5 seems to be near-steady as well as more significant than that from the other. The stability of methane NOC indicating from CH_4 conversion (Fig. 3) and yield of H_2 (Fig. 4), was possibly occurred from the change in acidity due to boron replacement. Resulting from that, 6Mo/H-[B]ZSM-5 can proceed the reaction steadily from TOS = 180 to the end of the reaction.

Table 2. Catalytic activities after 360 min TOS.

Samples	X_{CH4} (%)	Yield (mol%)				
		C_2	H_2	CO	C_6H_6	coke
6%Mo/H-ZSM-5	13.6	0.04	0.07	0.03	4.8	8.8
6%Mo/H-[B]ZSM-5	13.5	0.06	0.11	0.05	6.5	6.9

Table 2 summarizes the overall methane conversion (X_{CH4}) and product distribution for the 6%Mo/H-ZSM-5 and 6%Mo/H-[B]ZSM-5. The coke yields were determined from the amount of coke that had been left on the spent catalysts. The 6Mo/H-[B]-ZSM-5 had accepted 12.3 %wt of coke, corresponding to 6.9 mol%-CH_4. These are lower than those for the 6Mo/H-ZSM-5; 18.4%wt and 8.8 mol%, respectively. The less significant coke deposition onto the 6Mo/H-[B]-ZSM-5 is reasonably ascribed to lower acidity of Brønsted acid sites (BASs). According to the previous studies, the BASs of zeolites play catalytic roles not only in the aromatization of C_2 intermediates but also the coke formation [5,6]. Thus, the chemical modification of Brønsted acid sites by using boron instead of aluminum but by boron reduced the acidity of ZSM-5. It is known that a smaller atom can exist in coplanarity with three oxygen atoms, and this leads to a weaker and longer bond when forming with the fourth oxygen. Thus, the bridging OH of [B]ZSM-5 became an acid weaker than that in the [Al]ZSM-5 [6]. This qualitatively but reasonably explains show the lower coke yield and higher C_2 selectivity by the 6Mo/H-[B]ZSM-5.

4. CONCLUSION

The 6Mo/H-ZSM-5 and 6Mo/H-[B]-ZSM-5 did not show significant difference in catalytic activity toward the NOC of methane. Although the 6Mo/H-[B]-ZSM-5 catalyst exhibited slightly lower initial catalytic activity, it provided greater stability. Furthermore, the modification of Brønsted acid sites with boron instead of aluminum resulted in the suppression of coke formation and the higher yields of desired products. i.e., hydrogen, ethylene and benzene.

5. REFERENCES

[1] B. Wang, S. A-Suazo, Y. P-Torres, E. Nikolla, Advances in methane conversion processes, Catal. Today. 285 (2017) 147-158.

[2] J. J. Spivey and G. Hutchings, Catalytic aromatization of methane, Chem. Soc. Rev. 43 (2014) 792-803.

[3] S. Ma, X. Gua, L. Zhao, S. Scott, X. Bao, Recent process in methane dehydroaromatization: From laboratory curiosities to promising technology, J. Sci. Commun. 163 (2010) 51–59.

[4] Y. Xu, X. Bao, L. Lin, Direct conversion of methane under nonoxidative conditions, J. Catal. 216 (2003) 386-395.

[5] J-P. Tessonnier, B. Louis, S. Rigolet, M.J. Ledoux, C. P-Huu, Methane dehydro-aromatization on Mo/ZSM-5: About the hidden role of Brønsted acid site, Appl. Catal. A. 336 (2008) 79-88.

[6] H. Sheng, E.P. Scheiner, W. Zheng, R.F. Lobo, Non-oxidative coupling of methane to ethylene using Mo_2C/[B]ZSM-5, Chem, Phys. Chem. 19 (2018) 1–9.

[7] L. Wang, L. Tao, M. Xie, G. Xu, Dehydrogenation and aromatization of methane under non-oxidizing conditions, Catal. Lett. 21 (1993) 35-41.

[8] A.K. Aboul-Gheit, A.E. Awadallah, A.A. Aboul-Enein, A-L.H. Mahmoud, Molybdenum substitution by copper or zinc in H-ZSM-5 zeolite for catalyzing the direct conversion of natural gas to petrochemicals under non-oxidative conditions, Fuel. 90 (2011) 3040-3046.