Dehydroaromatization of Methane in the Absence of Oxygen over Modified W/HZSM-5 Catalyst

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Abstract

The direct conversion of methane to aromatics, mainly benzene without using oxygen, was studied. In prior, a comparison was conducted for the catalytic properties of W/USY, W/Al$_2$O$_3$, W/Hβ, and W/HZSM-5. Among all the support used, the W/HZSM-5 catalyst showed the best activity and stability with highest methane conversion of 8.4%, corresponding to aromatics selectivity of 97.54% at 973 K and 1 atm. Meanwhile, almost ~ 7% of methane was converted on the other W-supported catalysts, which were drastically deactivated. Further study was performed to investigate the role of acidity of the W/HZSM-5 catalyst. The acidic properties of the catalysts have undergone changes due to the introduction of Li ion. The catalytic properties for those catalysts with Li contents, including 3W/HZSM-5, 3W/Li-HZSM-5(10), 3W/Li-HZSM-5(12), 3W/Li-HZSM-5(46), and 3WLiZSM-5 catalysts were tested at 1073 K and 1 atm. The results demonstrated that the introduction of a certain amount of Li into the ZSM-5 catalyst influences the catalytic performance of dehydroaromatization of methane under the non-oxidative condition. Over W/HZSM-5, a maximum methane conversion achieved was 16%, but decreased considerably to 8% over 320 min. of time on stream. Furthermore, the corresponding aromatic selectivity dropped rapidly from 93% to 56%. While, over the 3W/Li-HZSM-5(10) catalyst which contains 74% of strong acid sites of the parent HZSM-5 resulted in a slight decrease in methane conversion from 18% to 12%, with corresponding to aromatics from 91% to 85%, that was observed after 320 min. of time on stream. However, in the case of more Li content was added, the activity of the catalyst decreased as shown those on the 3W/Li-HZSM-5(12), 3W/Li-HZSM-5(46), and 3W/Li-ZSM-5 catalysts. Also it was found that the catalyst performance could be improved by reducing the amount of the strong acid sites, but considerable reduction in the amount of acidic sites, particularly the Brönsted acid sites, is unfavorable for the non-oxidative methane dehydroaromatization. The 3W/Li-HZSM-5(10) catalyst is found to be suitable catalyst as it has the optimum Brönsted acid sites and consequently, gives the maximum methane conversion and selectivity to aromatics. These results suggest that Li modified W/HZSM-5 catalysts is bifunctional catalyst in which both W active sites and Brönsted acid sites of HZSM-5 support are crucial factors for good catalytic performance.

Introduction

The abundant natural gas available globally can be better utilized as alternative source of chemicals as it has predominantly employed as fuel today. Natural gas consists of primarily methane with varying proportions of ethane, propane, nitrogen and some impurities such as CO, H$_2$S or trace metals. The conversion of natural gas to more easily transportable fuels and valuable chemicals can be carried out using a partial oxidation of methane (POM) to methanol, methane oxidative coupling (MOC), and methane partial oxidation reactions [1]. In addition, a direct transformation of methane to more valuable hydrocarbons such as aromatics or C$_2$ hydrocarbons is a fascinating way for reasonable utilization of natural gas resources. In terms of oxidation process, there is a process involving non-oxidative reactions. Compared with the methane oxidative coupling (MOC) and the methane partial oxidation (POM) reactions, the advantages of the methane non-oxidative transformation process is that the selectivity to higher hydrocarbon products is high and the main product, benzene, is easier to separate from the methane feed. Wang et al. has indicated that many problems causing from the side

reaction such as methane complete oxidation can be avoided under non-oxidative reaction conditions [2]. The methane non-oxidative transformation has been extensively studied over transition metal ions (TMI), such as Mo, Fe, V, W, and Cr, Zn, Ga and Re by using HZSM-5 as well as MCM-22 zeolite as a support [3,4]. Previously, the interaction between the Mo species and HZSM-5 and their activity for methane dehydroaromatiztion has been studied by several researchers [5,6,7,8]. These studies indicate that there is an induction period during which the MoO_3 is reduced by CH_4 and transformed into Mo_2C. They suggested that the formed Mo_2C is responsible for methane activation. Meanwhile, the Brönsted acid sites of HZSM-5 are regarded to be responsible for the formation of aromatics. These results show that the acidity and channel structure of HZSM-5, as well as the location and state of Mo species on/in HZSM-5, are crucial factors in its catalytic performance [8,9]. Usually, it is well recognized that Zn/HZSM-5 and Ga/HZSM-5 catalysts are bifunctional (dehydrogenating and acidic functions). Thus, for a catalyst to give good catalytic performances for the aromatization of shortchain paraffins, it is necessary to have a good and proper match between dehydrogenating and acidic properties [10].

Previous work conducted by Zeng et al. [11] showed incorporation of Zn (or La) into the $W–H_2SO_4$ /HZSM-5 catalyst was found to markedly improve the DHAM activity and stability of the catalyst operating under relatively high temperatures. With incorporation of Zn (or Mn, La, Zr) into the W/HZSM-5 catalyst, highly active and heat-resisting W/HZSM-5-based catalysts were developed [12]. In the present work, the effects of supports on W based catalysts and the addition of Li ion into W/HZSM-5-based catalysts were investigated and correlated with the catalyst performance for the DHAM reaction.

Materials and Methods

Catalyst preparation
W supported zeolites (USY, Al_2O_3, Hβ, HZSM-5) were prepared by impregnation using a calculated amount of ammonium meta tungsten solution (($NH_4)_6W_{12}O_{40}.H_2O$). The W loading of these samples is 3 wt%. The impregnated samples were dried overnight at 373 K and calcined at 873 K for 4 hours. Afterward, the catalysts were pressed, crushed, sieved to between 35-60 mesh. A series of Li modified W/HZSM-5 was prepared by sequence method of ion exchange and impregnation. The partially Li-exchanged HZSM-5 was prepared by using mixtures of 1 M $LiNO_3$ and 1 M NH_4NO_3 solution with different ratios. While, for the fully Li-exchanged ZSM-5 catalyst was using 1 M $LiNO_3$. Subsequently, the samples were dried at 393 K overnight. Following the ion exchange, these samples were impregnated using certain amount of (($NH_4)_6W_{12}O_{40}.H_2O$) solution to obtain 3 wt. % W/Li-HZSM-5 catalysts. The catalysts code was varied based on the % mol of Li exchange on the catalysts. The amount of Li^+ exchanged into HZSM-5 was determined by ICP technique.

Catalyst characterization
Nitrogen adsorption (NA) was carried in a Thermo Finnigan surface area analyzer. The BET surface area and the pore volume were determined at 77 K. The TPD ammonia was employed to measure the catalysts acidity using a Micromeritics TPD/TPR/O analyzer. Initially, the catalyst sample was flushed in N_2 stream at 15 K/min up 873 K then cooled to 383 K. Next, the samples were saturated with pure ammonia at 373 followed by heating up to 873 K with He stream for 1 hour. The NH_3-TPD experiments were carried out from 373 to 873 K, with heating rate of 15 K/min. The number and strength of the catalyst acidity were then recorded.

Catalyst evaluation
The conversion of methane was carried out in a micro fixed-bed quartz reactor of 9 mm internal diameter in which 1 g of catalyst was charged. The feed gas comprised of CH_4 + 10% N_2 as internal standard were passed through the catalyst bed (containing 1 g of catalyst) at a space velocity of 1800 ml/(g.h), 973 – 1073 K, and atmospheric pressure. The reaction products were analyzed by an on-line GC (Hewlett-Packard 5890) equipped with Porapak Q, molecular sieve 5A, UCW 982, and DC 200 columns and a TCD.

Results and Discussion

Figure 1 compares the results of activity testing the conversion of methane to aromatics over W/HZSM-5, W/USY, W/Al$_2$O$_3$, and W/Hβ catalysts. The highest catalytic activity is found over W/HZSM-5 with maximum methane conversion of 8.4%. While, the maximum value of methane conversion over W/Hβ, W/USY, and W/Al$_2$O$_3$, was 7.83%, 7.46%, and 7.33%, respectively. For all the catalysts, the selectivity to aromatics shows a maximum at 40 min of the time on stream then decrease with further increase in time on stream. The highest selectivity to aromatics for W/HZSM-5, W/Hβ, W/USY, and W/Al$_2$O$_3$ catalysts were 97.54%; 98.23%; 58.95%; and 89.88%, respectively. Furthermore, it is also shown in Figure 1, that the selectivity of C$_2$ hydrocarbons increase significantly with the highest amount of C$_2$ as shown on W/USY catalyst. Simultaneously, a considerable increase in C$_2$ selectivity is observed when the aromatics selectivity decrease sharply. The selectivity of C$_2$ over W/HZSM-5 increased from 0.57 to 1.56% after 280 min time on stream, whereas for the W/Hβ, W/USY, W/Al$_2$O$_3$ catalysts increased in a range of 0.34 - 5.03% ; 1.00 - 6.45% ; 1.17 - 10.24% at the same reaction time, respectively. The increased in aromatics selectivity together with a decrease in C$_2$ selectivities are due to coke deposition in the catalysts. Table 1 shows the physicochemical properties of 3W supported zeolites. The different activities and stabilities exhibited by a series of the 3% W-based catalysts with different supports in the DHAM suggest that the physico-chemical properties of the catalyst support affect the performance of the catalysts. HZSM-5 possesses two-dimensional pore structure with a 10-membered ring. Its pore system consists of a straight Channel with pore diameter of 5.3 x 5.6 Å [4].
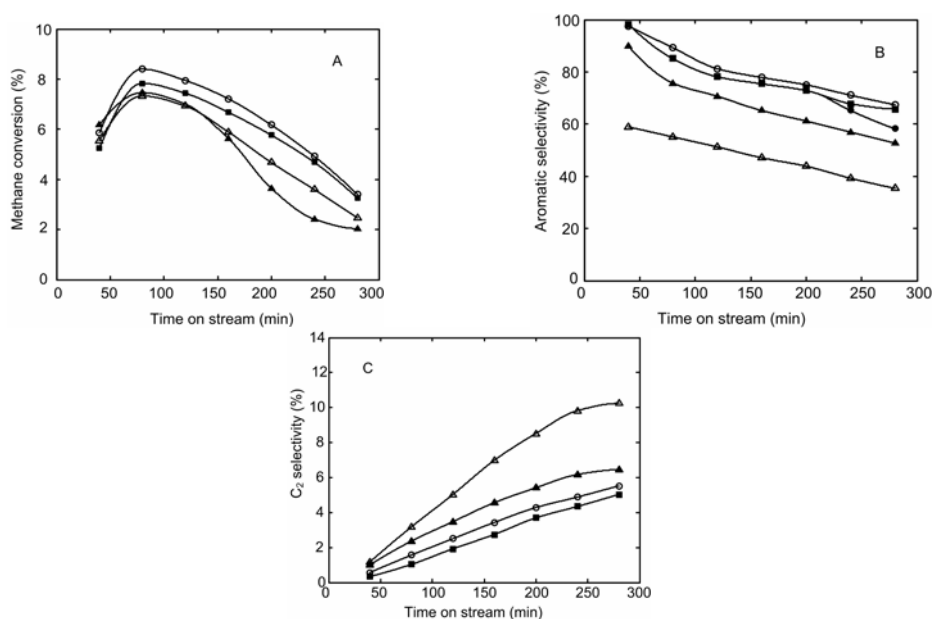

Figure 1: Methane conversion and products selectivity over 3 wt.% W loaded on different supports : (O)W/HZSM-5(Si/Al=30); (■)W/Hβ (Si/Al=25); (▲)W/USY(Si/Al=5.1);(△)W/Al$_2$O$_3$. Reaction conditions; T=973 K, GHSV=1800 ml/(g.h), 1 atm; Feed Gas = CH$_4$ + 10% N$_2$.

Table 1. Physicochemical properties of 3W supported zeolites

Sample	BET surface area (m^2/g)	Micropore volume (cm^3/g)
3W/Hβ	484	0.319
3W/USY	611	0.596
3W/Al$_2$O$_3$	124	0.283
3W/HZSM-5	363	0.232

The value of maximum methane conversion and aromatics selectivity are used to compare the performance of W based catalyst with different types of supports. The results give evidence that HZSM-5 is a good catalyst support used for methane dehydroaromatization reaction yielding the highest methane conversion and aromatic selectivity. Due to its shape-selectivity, HZSM-5 was selected for further study to investigate the relationship between acidity and activity of the catalyst for methane dehydroaromatization.
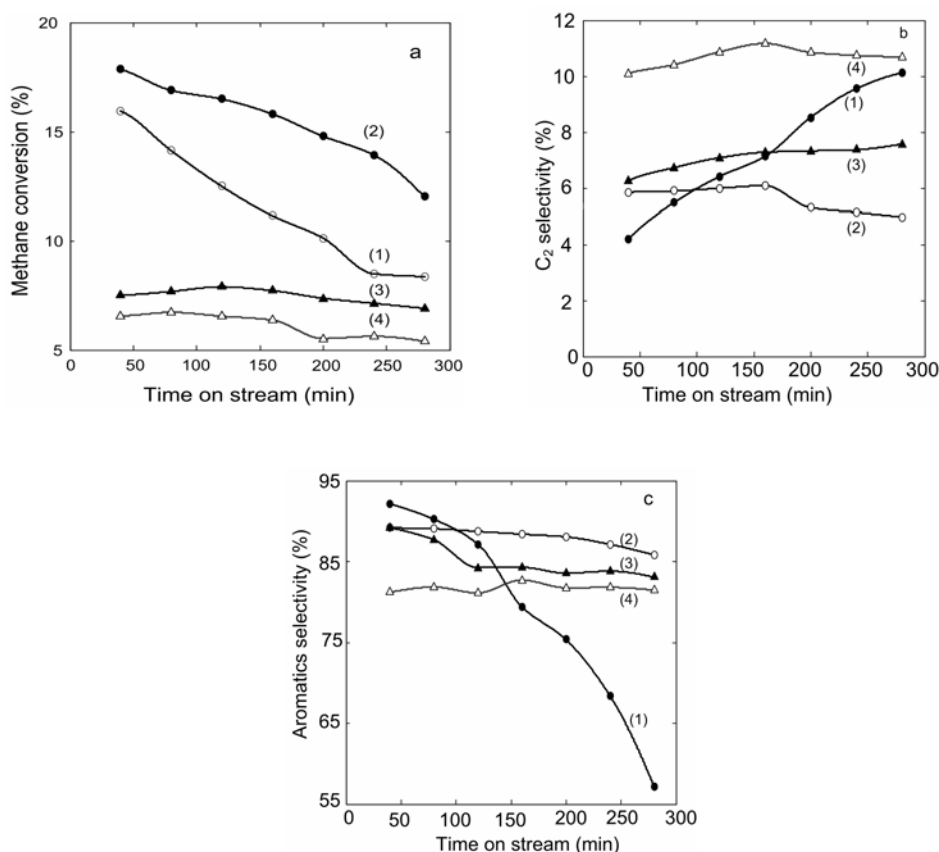

Figure 2: Results of catalytic testing for the conversion of methane to aromatics hydrocarbons in the absence of oxygen over (1) 3W/HZSM-5, (2) 3W/Li-HZSM-5(10), (3) 3W/Li-HZSM-5(12), (4) 3W/Li-HZSM-5(46) catalysts, respectively. Reaction conditions used were 1 atm, T= 1073 K,WHSV :1800 ml.g^{-1}.h^{-1}.(a) Methane conversion versus time on stream (b) C$_2$ selectivity vs time on stream (c) aromatics selectivity vs time on stream.

The effect of Li ion doping was studied to investigate the addition of alkali on the catalyst performance for dehydroaromatization of methane in the absence of oxygen. The reaction was conducted with the following reaction conditions: the methane gas feed flow rate of 1800 ml/(g.h), in the temperature of 1073 K under atmospheric pressure. Figure 2 shows the effect of Li ion on the catalytic performances of W based catalysts. The addition of Li led to an increase in methane conversion and aromatics selectivity but a slight decrease in C$_2$ hydrocarbons within 320 time on stream on the 3W/Li-HZSM-5(10) as compared catalyst without Li ion, 3W/HZSM-5. Nevertheless, in the case of more Li contents in the catalysts, 3W/Li-HZSM-5(12) and 3W/Li-HZSM-5(46), the catalytic activity is decreased significantly. Based on this result, it is suggested that modification of W/HZSM-5 with proper amount Li ion could promote the activity and stability the catalyst. Previously, Xiong et al. [12] reported that introduction of second metal ion such Mg^{2+} and Zn^{2+} resulted in the elimination of a large portion of the strong acids sites leading to improve activity and stability catalysts. In addition, the correlation between the activity of benzene formation in methane aromatization and the strong Brönsted acidity of Mo/HZSM-5 had been reported by Liu S., et al. [8]. The rates of aromatics on the Mo/HZSM-5 catalyst substantially depend on the SiO$_2$/Al$_2$O$_3$ ratios of the HZSM-5 used. It was found that maximum benzene formation was obtained on the Mo/HZSM-5 having SiO$_2$/Al$_2$O$_3$ ratios of 20–49, but substantially poor activities on those with SiO$_2$/Al$_2$O$_3$ ratios smaller and higher than 40. The results imply that the formation of benzene and the conversion of methane are attributed to existence of

proper amount the strong acidity of the catalyst. NH$_3$-TPD characterization of 3W/HZSM-5 and 3W/Li-HZSM-5 samples is presented in Table 2.

Table 2:   NH$_3$-TPD results of 3W/HZSM-5 and 3W/Li-HZSM-5 samples

Sample	Li$^+$ exchange (mol%)	Brönsted acid sites (mmol/g)	Relative amount of strong acid sites (Peak)*
3WHZSM-5	0	1.588	0.94
3W/Li-HZSM-5(10)	10	1.246	0.74
3W/Li-HZSM-5(12)	12	1.186	0.69
3W/Li-HZSM-5(46)	46	1.122	0.63

* = Relative amount of strong acid sites = amount of strong acid sites of modified catalysts/amount of strong acid sites of HZSM-5 (1.788 mmol/g).

Moreover, the NH$_3$-TPD investigation combined with the result of catalyst evaluation clearly indicated that the intensity and concentration of the Brönsted-acid sites have a pronounced effect on the catalytic dehydroaromatization of methane. From the NH$_3$-TPD results, the introduction of Li ion by ion exchange method decrease the amount of strong acidity. The amount of strong acid sites decrease with an increasing Li content due to Li ions replacing the H$^+$ positions in the Si-OH-Al group of Brönsted-acid sites. Maximum methane conversion decreased from 16 to 8% with corresponding selectivity to aromatics decreased from 93 to 56% at 320 min time on stream over 3W/HZSM-5. While, maximum methane conversion decreased from 18 to 12% with corresponding selectivity to aromatics decreased from 91 to 12% at 320 min time on stream over 3W/Li-HZSM-5(10) indicating doping of the certain Li ion enhance the lifetime of catalyst. It has been reported that coke formation was the main reason for catalyst deactivation leading to decrease the catalyst activity [13,14,15]. The coke formation on the 3W/HZSM-5 catalyst could be observed by the darkening catalyst after reaction for 320 min. It was found that there is a close correlation between the activity and Brönsted acid sites [8]. The Brönsted acid sites on the catalyst were responsible for the formation of aromatics but an excess of Brönsted acid sites led to severe coke formation. The TPD result also showed about 1.588 mmol/g or 94% of the strong Brönsted acid sites exist on the 3W/HZSM-5 as compared to the parent HZSM-5. Further addition of Li content reduced the amount of Brönsted acid sites. The deposition of coke on the 3W/HZSM-5 catalyst might be related to Brönsted acid sites of catalyst. The deactivation of the catalyst resulted in reduced pore volume leading to suppression the selectivity to aromatics while increase the selectivity of ethylene. The correlation between Brönsted acid sites and methane aromatization been reported on Mo/HZSM-5 [5,8]. It was suggested that Brönsted acid sites of the HZSM-5 supports may bifunctionally promote not only the methane activation on the Mo carbide sites of Mo/HZSM- 5 catalysts, but also a further oligomerization of the dissociative CHx surface species towards the primary products such as ethene, which are effectively converted into benzene and naphthalene on the Mo/HZSM-5 catalysts.

Conclusion

The direct conversion of methane to aromatics such as benzene and naphthalene has been studied on a series of W-supported catalysts using HZSM-5, Hβ, USY and Al$_2$O$_3$ as the supporting materials and also on Li modified W/HZSM-5 catalysts. Among all the supports used, the HZSM-5 supported W catalysts exhibit the highest yield of aromatic products, achieving over 97% total selectivity of the hydrocarbons at 8.4% methane conversion at 973 K and 1 atm with GHSV of 1800 ml/g.h. By contrast, less than 7.8% of methane is converted to hydrocarbons products containing aromatics on the other W-supported catalysts, which are drastically deactivated, due to serious coke formation. Further investigation on the activities of Li modified W/HZSM-5 catalysts shows that a close relationship exists between the strong acidity and the methane conversion/aromatization activity. It was found that maximum benzene formation was obtained on the Li modified W/HZSM-5 having 1.246 mmol/g or 74% of the original strong acid sites of the parent HZSM-5, but substantially poor activities on those with more Li ion content in the catalysts ratios. The catalytic activity is directly proportional to the number of Brönsted acid sites on the surface which play a key role in methane dehydrogenation and aromatization. Therefore, our present activity testing combined with the NH$_3$-TPD results strongly supports the idea that W/HZSM-5 is a bifunctional catalyst. These sites are responsible for the oligomerization and dehydrocyclization of the primary ethylene product to form aromatics.

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