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Conversion of mixtures of methane and acetylene or ethylene into higher molecular weight hydrocarbons over metal-loaded and unloaded HZSM-5 zeolite catalysts

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Abstract

A mixture of acetylene and hydrogen was reacted over HZSM-5 zeolite catalyst at 200 °C to produce ethylene. A stream containing ethylene and methane was then reacted over gallium-loaded and copper-loaded ZSM-5 to produce higher molecular weight hydrocarbons. The effect of co-feeding methanol or chloroform on the product distribution was also investigated. On the other hand, a mixture of acetylene and methane was reacted over metal-loaded ZSM-5 catalysts to produce higher molecular weight hydrocarbons with a carbon number of five and more. Palladium, platinum, and nickel were among the transition metals tested.

Keywords: Methane conversion; Acetylene conversion; Ethylene conversion; Modified HZSM-5

1. Introduction

Methane conversion into higher molecular weight hydrocarbons has been the focus of many researchers in recent decades. Olah [1] was the first to convert methane by using a super acid “magic acid” that contained a mixture of fluorosulfuric acid and antimony pentafloride (HSO_3F/SbF_5). The yield was low and the acid system was depleted very quickly.

In their work Weckhuysen et al. [2] converted methane into aromatics (benzene, toluene, and naphthalene) over different transition metal-loaded ZSM-5 zeolites (Fe, V, W, Mo, and Cr) at a reaction temperature of 750 °C. Solymosi et al. [3] investigated the reaction of methane over supported and unsupported Mo-based catalyst at high temperature (700 °C). They noticed that molybdenum metal and oxides interacted strongly with methane at 700 °C to give H_2, H_2O, CO_2, and a trace amount of ethane. When these compounds were contacted with ZSM-5, ethane, ethylene, and benzene were formed. Shu et al. [4] studied the promotional effect of Ru on the dehydrogenation and aromatization of methane in the absence of oxygen over Mo/HZSM-5 catalysts. They reported that methane can be activated in the absence of oxygen over Mo/HZSM-5 catalyst with a conversion of 6–8% and a selectivity of aromatics to 90% at 700 °C.

In another process developed by Allenger et al. [5] methane reaction with acetylene was reported to take place over a solid acid catalyst containing fluoride to produce isobutene. Timmons et al. [6] reported the reaction of acetylene over nickel or cobalt-containing zeolite catalyst in the presence of a hydrogen donor co-reactant to produce higher molecular weight hydrocarbons. White et al. [7] have developed a process to

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react acetylene with itself or with any of the following compounds: hydrogen, methane, and ethane over zeolite catalyst. An aromatic rich stream containing 10 wt.% benzene, toluene, and xylene was obtained.

In this work, the ultimate goal is to convert methane into higher molecular weight hydrocarbons. Methane is first converted into acetylene via a process described elsewhere [8]. Acetylene is then either mixed with methane and converted directly into higher molecular weight hydrocarbons over metal-loaded zeolites or hydrogenated into ethylene over HZSM-5 where ethylene in a feed mixture comprising methane is then reacted over a catalyst to produce higher molecular weight hydrocarbons. The effect of co-feeding chloroform or methanol with the feed mixture on the product distribution is also investigated.

2. Experimental

The experimental work was conducted using a stainless steel fixed bed reactor system described elsewhere [9]. The reactor system was operated under continuous flow and it could be operated under a range of pressures starting from atmospheric up to 1500 psi and a range of temperatures of 0–1200 °C. The reactor tube and the piping system were made of 316-type stainless steel. Copper was avoided as a material of construction because of its high reactivity with acetylene.

In this work, different mixtures of gases were fed to the reactor at different operating conditions to achieve certain product distribution in each case. A mixture of acetylene and hydrogen was reacted over HZSM-5 with silica to alumina ratio of 280 at a temperature of 200 °C and atmospheric pressure to produce ethylene. The feed mixture, which was diluted with nitrogen, has a molar composition of 15.7, 6.2, and 78.1% hydrogen, acetylene, and nitrogen, respectively and was fed to the reactor at a total weight hourly space velocity (WHSV) of 3.24.

On the other hand methane and ethylene were fed to the reactor in a molar ratio of 6–1 at WHSV of 0.41, atmospheric pressure, and a reaction temperature of 300 °C. The catalyst (HZSM-5 with silica to alumina ratio of 30) was loaded with 1.48 wt.% gallium. Different experiments were conducted: in one case the reaction was carried out over the (Ga/ZSM-5) catalyst feeding only methane and ethylene with no additives. In another experiment the effect of adding methanol to the feed was investigated. A small amount of methanol was added to the feed by allowing ethylene to bubble through methanol then mix with methane before entering the reactor. Methanol was introduced to the reaction mixture in an attempt to generate carbinium ions which help to initiate the reaction and produce heavier components.

The effect of co-feeding chloroform on the product distribution was also investigated. Chloroform was introduced to the feed in two ways: (a) bubbling ethylene thorough the chloroform before mixing with methane; (b) saturating γ-alumina with chloroform and allowing ethylene to pass through the saturated γ-alumina column before mixing with methane. Chloroform was introduced to the feed mixture in an attempt to increase the acidity (Lewis acidity) since aluminum trichloride is known to have Lewis acid sites. In another experiment the catalyst (Ga/ZSM-5) was reduced with hydrogen and tested for activity, feeding only methane and ethylene.

Copper-loaded zeolite (Cu/ZSM-5) was also investigated for the reaction of methane and ethylene. The catalyst was loaded with 1.34 wt.% copper. The activity tests were conducted feeding methane and ethylene in one case and co-feeding chloroform with methane and ethylene in the other one. Methane and ethylene were fed to the reactor in a molar ratio of 6–1, WHSV of 0.41, atmospheric pressure, and reaction temperature of 300 °C.

The effect of loading HZSM-5 (30) catalyst with different transition metals such as: palladium, platinum, and nickel was also investigated. The catalyst was loaded with 0.5 wt.% palladium, 0.5 wt.% platinum, or 3 wt.% nickel. The feed consisted of methane and acetylene in a molar ratio of 6–1, WHSV of 1, and a reaction temperature of 400 °C.

Since the feed mixture contained acetylene, special safety precautions were taken into consideration. Copper, which is highly reactive with acetylene, was avoided as a material of construction. The acetylene cylinder was secured in a safe place avoiding heat sources and mechanical shocks. The experimental setup was checked for leaks before each experiment. This is an important measure because of the wide range of flammability of acetylene (2.5–100%). Moreover, acetylene partial pressure in the feed mixture was kept below 25% in all cases.

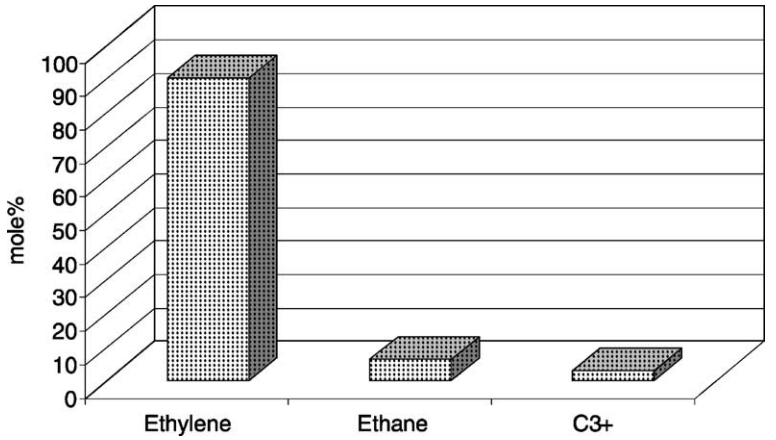

Fig. 1. Product distribution for the reaction of acetylene with hydrogen over HZSM-5 (280) at TOS = 15 min, $T = 200\,^{\circ}C$, and $P = 1$ atm.

3. Results and discussion

3.1. Acetylene reaction into ethylene

Fig. 1 shows the product distribution for the reaction of acetylene with hydrogen over HZSM-5 catalyst. The feed mixture comprises acetylene, hydrogen, and nitrogen with a molar composition of 6.2, 15.7, and 78.1%, respectively. Ethylene was the predominant product; in addition, ethane and small amounts of some other higher molecular weight hydrocarbons were produced. At the time that 90% of the product stream was ethylene; ethane formed only (6.5%) of that stream. Production of ethylene from this step can be useful for the reaction of ethylene with other additives over metal-loaded zeolite catalysts as will be discussed later in this paper.

Fig. 2 shows the ethylene selectivity with respect to acetylene conversion. High ethylene selectivity was achieved throughout the course of the experiment. Eighty five percent selectivity for ethylene was achieved at acetylene conversion of 64%. When acetylene conversion dropped to 49% at the end of the experiment as a result of partial deactivation of the catalyst, ethylene selectivity was 80%.

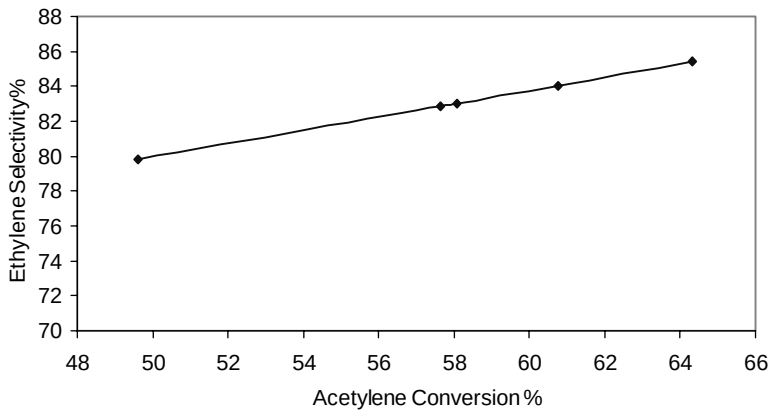

Fig. 2. Ethylene selectivity decrease with acetylene conversion decrease as a result of partial deactivation of the catalyst for the reaction carried out over HZSM-5 with silica to alumina ratio of 280, $T = 200\,^{\circ}C$, $P = 1$ atm.

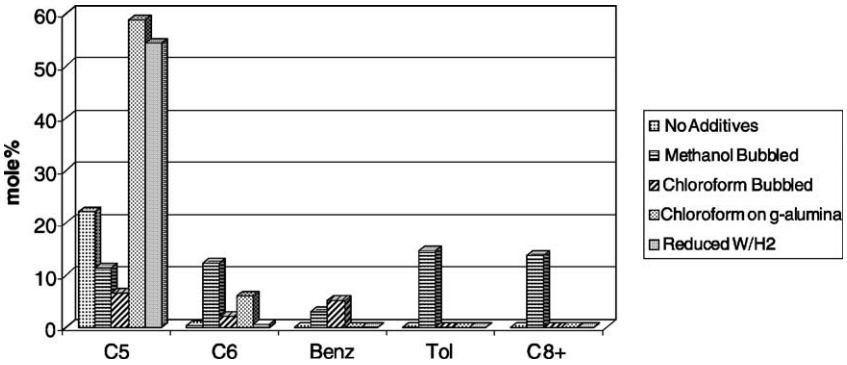

Fig. 3. A comparison of the product distribution for the heavy components for the reaction of methane and ethylene with different additives over Ga/ZSM-5, TOS = 15 min, $T = 300\,^{\circ}C$, $P = 1$ atm.

3.2. Ethylene reactions into hydrocarbons

The product distribution of the reactions carried out over gallium-loaded zeolite (Ga/ZSM-5) is shown in Figs. 3 and 4. The reactions produced heavy products (C_5 to C_8^+) as well as lighter products (C_2 to C_4) in addition to hydrogen in many cases. As can be seen from Figs. 3 and 4, introducing chloroform into the feed through the γ-alumina saturated column has significantly increased the percentage of C_5 in the products. About 22% of the products in the absence of chloroform in the feed are C_5, but once chloroform is introduced this number jumps to 59%. Reducing the catalyst with hydrogen showed a similar effect on the production of C_5. On the other hand introducing chloroform into the feed did not show a significant effect in the production of heavier products such as benzene, toluene, C_7, and C_8^+, however it showed a slight effect in producing C_6 hydrocarbons. In all cases a high ethylene conversion (99%) was achieved, however, no methane was converted.

When methanol was co-fed to the reactor instead of chloroform, a significant amount of heavy components was produced. Although the percentage of C_5 in the product stream was lowered when methanol has been introduced to the feed, a significant increase in the production of heavier components such as C_6, toluene, and C_8^+ has been achieved. About 41% of the products are C_6 to C_8^+ when methanol was introduced to the feed, compared to 0% when there was no methanol in the feed. Although methanol is known to convert to dimethylether (DME) over ZSM-5, no DME was detected in the product stream. It is believed that any DME formed was converted into other forms of

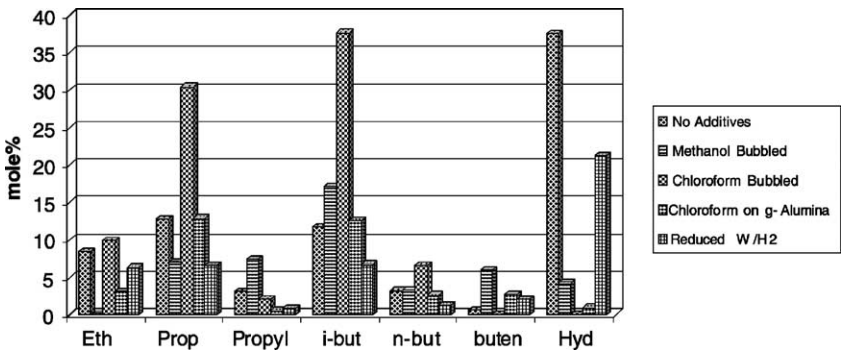

Fig. 4. A comparison of the product distribution for the light components for the reaction of methane and ethylene with different additives over Ga/ZSM-5, TOS = 15 min, $T = 300\,^{\circ}C$, $P = 1$ atm.

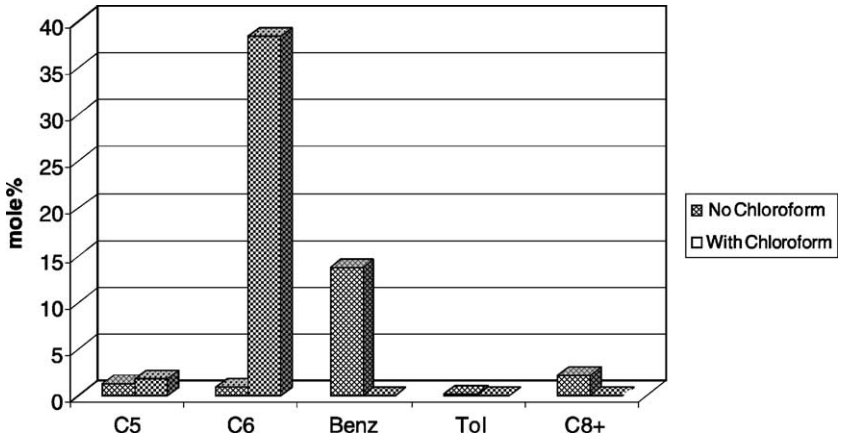

Fig. 5. A comparison of the product distribution for the heavy components for the reaction of methane and ethylene over Cu/ZSM-5 catalyst in the presence and absence of chloroform in the feed, TOS = 15 min, $T = 300\,^{\circ}C$, $P = 1$ atm.

hydrocarbons (aromatics, olefins, etc.). A high ethylene conversion (99%) was also achieved at the time that no methane was converted.

One can obviously see that the addition of chloroform to the feed gives the highest percentage of heavy components in the products (64%) most of it is C_5. On the other hand, introducing methanol into the feed will give a little lower—but still significant-percentage of the heavy components (55%) but it gives better product distribution (more C_6, toluene, and C_8^+).

Another set of experiments was conducted using a copper-loaded zeolite (Cu/ZSM-5). The results shown in Fig. 5 demonstrate that these reactions are capable of producing some heavy components. When no chloroform was co-fed to the reactor, benzene and small amounts of C_5, C_6, and C_8^+ were produced. On the other hand when chloroform was introduced, the amount of C_6 in the product stream increased significantly from 0.88 to 38.4% but no benzene, toluene, or C_8^+ were detected. A high ethylene conversion (99%) was obtained and no methane was converted.

3.3. Acetylene reactions into hydrocarbons

Fig. 6 shows the results obtained from reacting methane and acetylene with a molar ratio of 1–6 over HZSM-5 and metal-loaded HZSM-5 at a temperature of 400 °C and atmospheric pressure. As mentioned earlier, the catalyst was loaded with Pd (0.5 wt.%), Pt (0.5 wt.%), or Ni (3 wt.%). The results show that palladium-loaded ZSM-5 produced the highest percentage of heavy components (C_5 to C_8^+). Eighty percent of the product stream is C_5 to C_8^+ of which 31% is C_8^+. Significant amounts of toluene, benzene, and C_6 are also present in the product stream. This shows a significant improvement over the performance of non-loaded HZSM-5. As shown in Fig. 6, heavy components were produced when reacting acetylene over non-loaded HZSM-5, however, lower amounts of C_5 to C_8^+ (62%) were produced.

Nickel loaded zeolite (Ni/ZSM-5) also showed a better performance than that of the non-loaded HZSM-5 (30). Significant amounts of benzene, toluene, and C_8^+ were produced. Sixty eight percent of the product stream is C_5 to C_8^+, which is consistent with work reported in the literature. As an example Timmons et al. reported that 68.8% of the product stream to be C_5 or higher. They reacted acetylene over Ni (13 wt.%)/ZSM-5/Al_2O_3. When water and hydrogen were co-fed with acetylene they reported higher percentage of the heavy products in the product stream. Platinum-loaded zeolite (Pt/ZSM-5) was tested, and heavy components such as benzene, toluene, and C_8^+ were produced, however the percentage of these components in the product stream (43%) is much less than that obtained when using palladium-loaded HZSM-5 or non-loaded HZSM-5.

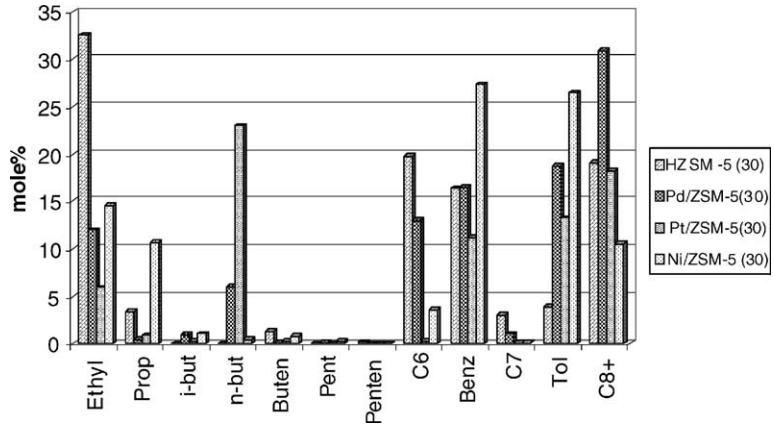

Fig. 6. A comparison of the product distribution for the reaction of methane and acetylene over different metal-loaded HZSM-5, TOS = 15 min, $T = 400\,^{\circ}C$, $P = 1$ atm.

Fig. 7 shows the comparison of the conversion of acetylene over time on stream for each type of the catalysts used. Palladium, platinum, and Ni-loaded pellet form of the ZSM-5 showed relatively prolonged time of high conversion. For the first 3 h and 15 min acetylene conversion was almost 100%, whereas this number dropped to 37% for Ni-loaded ZSM-5, 44% for Pd-loaded ZSM-5, and 53% for Pt-loaded ZSM-5 at the last hour of operation (4.25 h time on stream). On the other hand non-loaded HZSM-5 showed a high conversion (100%) at the first hour of operation then it decreased gradually to reach 41% at the end of the experiment. The powder form of the ZSM-5, however, deactivated faster than the pellet form. After only 2 h of operation, acetylene conversion dropped to 22% and lower.

The average carbon number data for the product streams for the different types of catalysts used are shown in Fig. 8. The non-loaded powder form of the ZSM-5 produced heavier components during the first hour of operation than all other catalysts. Pd-loaded ZSM-5 produced components with the highest average carbon number among the pellet form metal-loaded ZSM-5 catalysts tested. A comparison of the

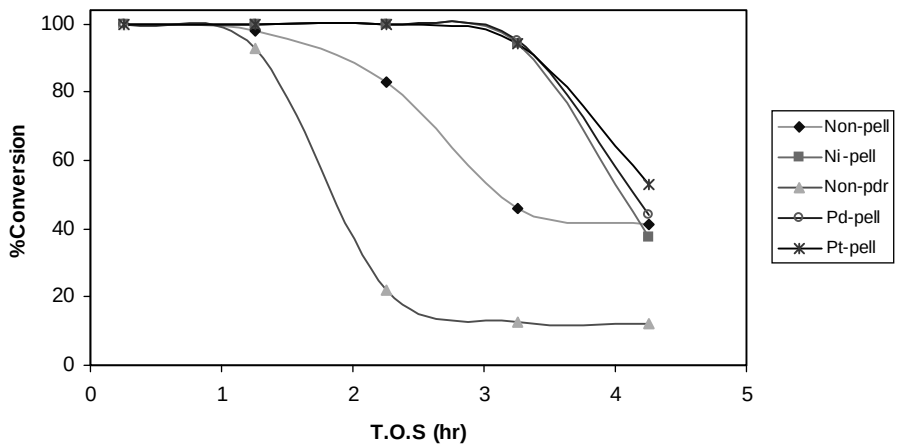

Fig. 7. Acetylene conversion over different metal-loaded and non-loaded ZSM-5 catalysts, $T = 400\,^{\circ}C$, $P = 1$ atm.

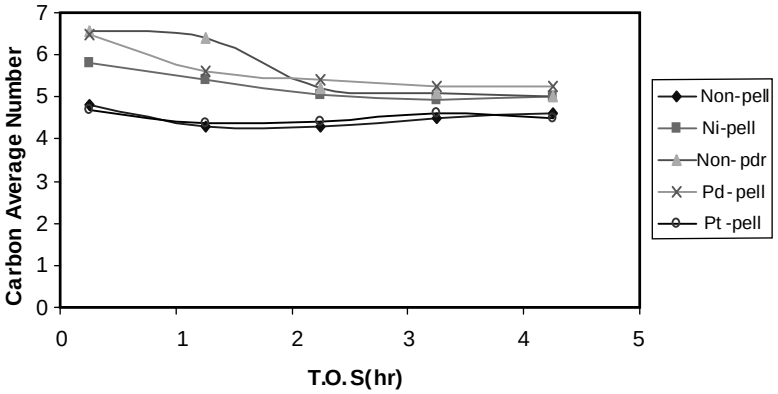

Fig. 8. Average carbon number for product streams for different metal-loaded and non-loaded ZSM-5 catalysts, $T = 400\,^{\circ}\mathrm{C}$, $P = 1\,\mathrm{atm}$.

performance of the catalysts used, based on conversion and average carbon number of the products, shows that Pd-loaded ZSM-5 is the catalyst with the best performance.

4. Conclusions

Acetylene reacted with hydrogen over HZSM-5 at 200 °C. The reaction produced ethylene with high selectivity (85%). A mixture of methane and ethylene or acetylene was reacted over HZSM-5 and different metal-loaded HZSM-5 catalysts. The reaction produced high molecular weight hydrocarbons with a carbon number of five and more. Among the different metal-loaded catalysts tested, Pd/ZSM-5 showed an improved performance in terms of the product distribution and conversion over all the other loaded and non-loaded HZSM-5 catalysts.

With gallium-loaded HZSM-5, introducing chloroform or methanol into the feed containing methane and ethylene increased the fraction of heavy components in the product stream when compared with products from HZSM-5.

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