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Co-conversion of Ethane and Methanol into Higher Hydrocarbons over Ga/H-ZSM-5, Mo/H-ZSM-5 and Ga-Mo/H-ZSM-5

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Abstract Ethane and methanol are converted simultaneously over Ga/H-ZSM-5, Mo/H-ZSM-5 and Ga-Mo/H-ZSM-5 to produce light olefins and aromatics. The presence of methanol in the reactant stream is intended to facilitate activation of ethane following literature reports on co-conversion of methane and methanol. However, the conversion of ethane actually decreases significantly when methanol is present. To gain insight into mechanistic details, ^{13}C-labeled methanol is co-converted with unlabeled ethane. These isotopic labeling studies show that carbon atoms from ethane and methanol are mixed in the products and in the carbonaceous compounds deposited on the catalysts. This indicates that both reactants take part in the formation of the hydrocarbon pool, which is the origin of all products.

Keywords Ethane conversion · MTH · Co-conversion · Mo/H-ZSM-5 · Ga/H-ZSM-5

1 Introduction

Natural gas is often produced at remote places and needs to be transported over large distances. This has proved to be a challenge. The gas can be transported in pipelines, which requires massive investments and maintenance, or alternatively it can be compressed or liquefied, but these processes consume a lot of energy. Therefore some of the produced natural gas is still being flared at the well site, whereby valuable products are lost and a considerable amount of CO_2 is emitted to the atmosphere. In the future, flaring of natural gas will most likely be banned or at least extremely costly, so it must be circumvented. As a consequence it could be very attractive to convert natural gas into valuable and easily transportable products at the well site.

One way of exploiting the low-molecular-weight hydrocarbons in the natural gas is by non-oxidative catalytic conversion into olefins or aromatics over metal-containing acidic zeolites [1, 2]. These reactions are endothermic and the thermodynamic equilibrium does not favor the desirable products unless the temperature is relatively high. When the reaction temperature is increased, the possibility of coking the catalyst is also increased, so an intermediate temperature is used, where the conversion is reasonably high while coking is suppressed. A possible way of circumventing these temperature restrictions is by activating the hydrocarbons by the addition of suitable compounds to the reactant stream. Several research groups have studied this approach, e.g., activation of methane by addition of various alkanes [3–6], alkenes [7–10], or light gasoline [11].

In another well-investigated reaction, hydrocarbons are produced by converting methanol into gasoline (MTG) or into olefins (MTO) over an acidic ZSM-5 zeolite catalyst [12–14]. This reaction is exothermic and is typically performed at 350–400 °C.

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A combination of the non-oxidative dehydroaromatization of alkanes and the methanol conversion might prove useful, since the heat produced in the exothermic methanol conversion can be exploited in the endothermic hydrocarbon aromatization. In principle, a thermoneutral reaction can be obtained in this way. The working hypothesis is that the alkane is activated by a combination of the dehydrogenating metal sites and the methanol generated hydrocarbon species on the catalyst [15].

Several research groups attempted to use methanol to promote the conversion of alkanes over different zeolite catalysts in cracking as well as aromatization reactions. Nowak and co-workers [16, 17] studied the methanol activated cracking of hydrocarbons by co-converting methanol with hydrocarbons like *n*-decane, *n*-hexane, cyclohexane, naphta, *n*-butane, and C_4 olefins over different Fe-containing modified H-ZSM-5 catalysts. The main products in these reactions were olefins. In another series of studies, Safronova et al. [18–24] co-converted methanol with a mixture of propane and butane over H-ZSM-5, and also observed an increase in the production of olefins when methanol was present. Methanol was also used by Chang et al. [25, 26] to improve the catalytic cracking of *n*-hexane over an H-ZSM-5 zeolite.

In a different study, Choudhary et al. [15] investigated the co-conversion of methane and methanol over Ga-, Zn-, In-, and Mo-modified H-ZSM-5 zeolites in the production of olefins and aromatics. Choudhary et al. reported that the conversion of methane was highly promoted by the presence of methanol in the feed. At conditions where methane by itself was not converted at all, it converted readily with methanol present. In fact, methane and methanol were converted in equimolar amounts.

This work by Choudhary et al. prompted us to investigate the possible activation of ethane by co-conversion with methanol over metal-containing H-ZSM-5 catalysts.

2 Experimental

2.1 Catalyst Preparation

The NH_4-ZSM-5 zeolite obtained from Zeolyst (CBV3024E, Si/Al = 15) was calcined at 550 °C for 4 h to obtain the acidic form. The zeolite was subsequently impregnated by the incipient wetness technique using aqueous solutions of $Ga(NO_3)_3 \cdot xH_2O$ and/or $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, dried overnight at 110 °C, and calcined at 550 °C for 4 h. The catalyst powder was pelleted, crushed, and sieved to obtain the desired particle size of 180–355 μm. The prepared catalysts contained 3 wt% Ga, 3 wt% Mo, and 2 wt% Ga + 2 wt% Mo, respectively.

2.2 Catalytic Tests

The catalytic tests were carried out with 500 mg of catalyst in a plug flow quartz reactor with an inner diameter of 3.7 mm. All the catalysts were pretreated at 550 °C prior to test. The Ga/H-ZSM-5 catalyst was pretreated in a flow of He for 2 h, while the molybdenum containing catalysts were pretreated in a H_2/CH_4 mixture (6% H_2) for 4 h to produce the catalytically active molybdenum carbide [15]. Tests were carried out at atmospheric pressure and at an oven temperature of 500 °C. The flow of ethane was 590 mL(SATP)/h. A uniform stream of methanol ($\mathrm{WHSV} = 0.16\ \mathrm{g\,g^{-1}\,h^{-1}}$) was obtained by leading 550 mL(SATP)/h of He through a bubble flask containing methanol at room temperature followed by another flask kept at 16 °C. The product stream from the reaction was analyzed by an online HP6890A gas chromatograph equipped with a TCD and an FID connected in series. The conversion of ethane was calculated from the TCD using Ar as an internal standard and the conversion of methanol was 100% in all runs. When ^{13}C-labeled methanol was used, gas samples were taken out manually through a septum immediately after the oven using a gas syringe of 1 mL. These gas samples were analyzed by GC–MS (Agilent 5975 MSD/6850 GC) to identify the distribution of labeled and unlabeled carbon atoms in the products.

2.3 Dissolution of the Catalyst

In order to analyze the carbonaceous compounds deposited on the catalysts the zeolites were dissolved in hydrofluoric acid after the catalytic tests using a method introduced by Guisnet and co-workers [27]. About 100 mg of the spent catalyst was placed in a closed teflon vial, 2 mL of 20% HF was added, and the zeolite was left to dissolve for 30 min. The liberated carbonaceous deposits were extracted by adding 1 mL of CH_2Cl_2 and analyzed by GC–MS.

3 Results and Discussion

The catalytic experiments are designed to resemble the methane and methanol co-conversion experiments performed by Choudhary et al. [15].

The Ga/H-ZSM-5 catalyst shows an ethane conversion of around 4% under the chosen test conditions (Fig. 1) with no methanol present. When methanol is added to the feed, the conversion drops significantly to around 2%. Thus, the conversion of ethane is apparently not increased by the presence of methanol; in fact, the opposite seems to be the case. The same tendency is observed for the Mo/H-ZSM-5 and Ga-Mo/H-ZSM-5 catalysts; especially

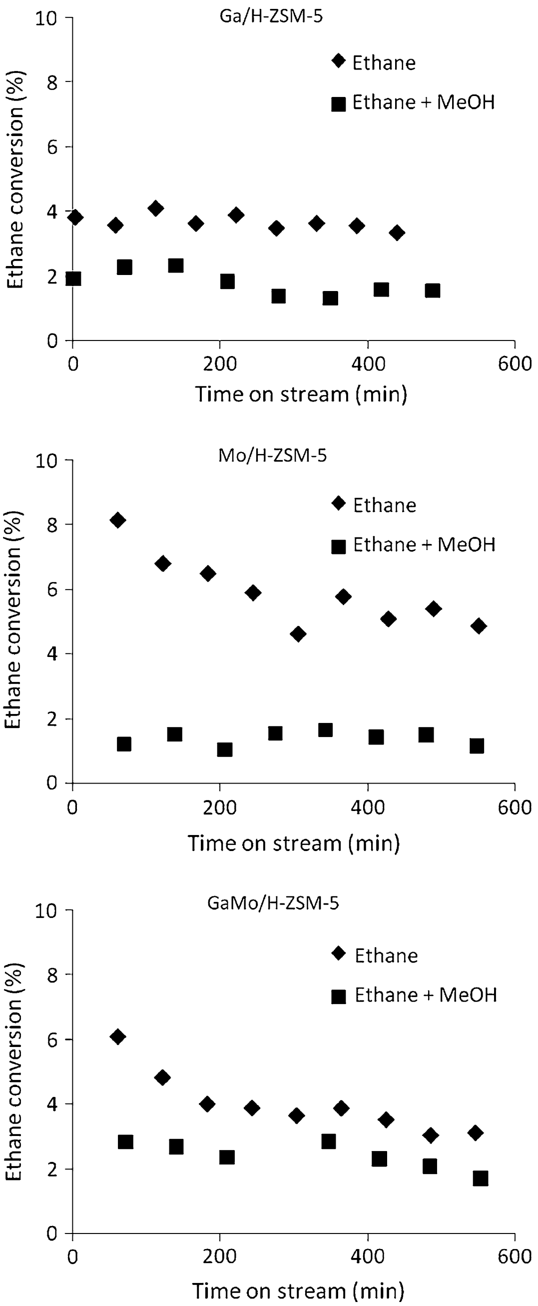


Fig. 1 Conversion of ethane, with and without methanol present ($T = 500$ °C, GHSV(ethane) = 1,180 $\mathrm{cm^3\ g^{-1}\ h^{-1}}$, GHSV(He) = 1,100 $\mathrm{cm^3\ g^{-1}\ h^{-1}}$, WHSV(MeOH) = 0.16 $\mathrm{gg^{-1}\ h^{-1}}$)

in the case of Mo/H-ZSM-5, the presence of methanol suppresses the conversion of ethane significantly.

The product selectivities for the co-conversion of ethane and methanol and for the conversion of the two reactants alone over Ga/H-ZSM-5 are shown in Fig. 2. The selectivities are relatively constant throughout the entire test period. The main products in the reactions are aromatics and small olefins. The presence of methanol induces production of heavier aromatics and more methane compared to when ethane is converted alone. It is interesting to note that the reaction does not produce aliphatics larger than C3 in detectable amounts. When methanol is converted alone, only insignificant amounts of ethane are produced. The decrease in the conversion of ethane is therefore not due to production of ethane from methanol.

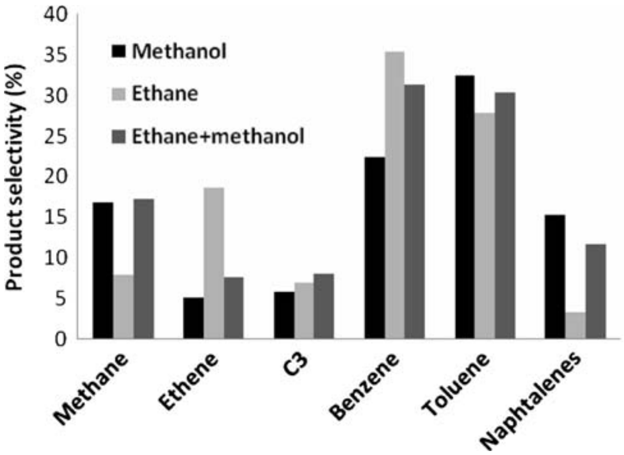


Fig. 2 Product selectivities in the conversion of methanol, ethane and ethane + methanol over Ga/H-ZSM-5 after at 500 °C, time on stream = 200 min

There could be several possible reasons for the decrease in ethane conversion in the presence of methanol. We believe that the most plausible explanation is that methanol and ethane are competing for the same catalytic sites. Ethane needs a combination of a dehydrogenating metal site and an acidic site on the zeolite to convert into aromatics; however methanol and hydrocarbon species generated from methanol are also able to bind to the metal sites, leaving fewer sites to convert ethane. Methanol is much more reactive than ethane or ethene, and is therefore converted at the inlet of the reactor, whereas ethane is converted throughout the entire catalyst bed. Due to the relatively high reaction temperature (500 °C) methanol is converted immediately, and there will not be any methanol present in the lower part of the reactor. However, methanol is converted to a range of products (small olefins and aromatics) which might be able to promote the conversion of ethane [7]. Even though these species might activate ethane, it is apparently not enough to make up for all the active sites occupied by the conversion of methanol.

Another factor that might be responsible for the suppressed ethane conversion is that methanol induces heavy coking of the catalyst, mainly at the inlet. This will naturally deactivate the catalyst and could lead to a lower conversion. However, Fig. 1 shows that the catalyst does not deactivate faster when methanol is present, within the timescale studied. The fact that the initial conversion is much lower when methanol is present supports the

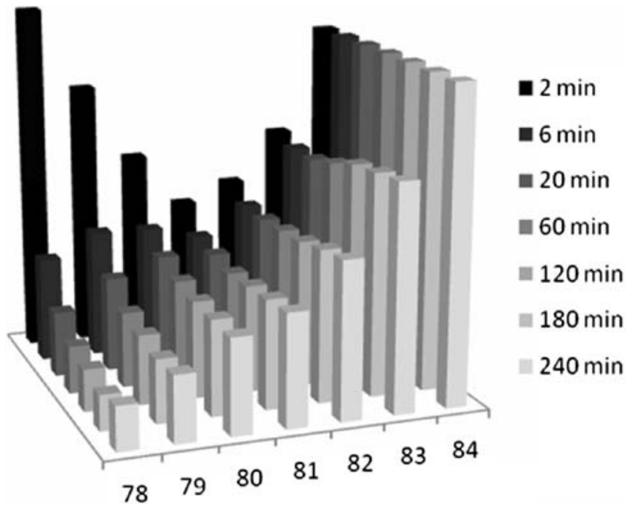


Fig. 3 Mass spectra of benzene, produced at different reaction times in a co-conversion experiment of unlabeled ethane and ^{13}C-labeled methanol over Ga/H-ZSM-5 at 500 °C. Normalized with respect to M = 84

hypothesis described above, that methanol and ethane simply compete for the same catalytic sites.

To trace if the carbon atoms in the products originate from ethane or methanol, co-conversion of unlabeled ethane and ^{13}C-labeled methanol was performed over Ga/H-ZSM-5. Gas samples were taken out from the product stream at different reaction times and analyzed by GC–MS. Figure 3 shows the mass spectra of benzene produced after different reaction times. There is a clear tendency, that in the first few minutes there is a high degree of ^{12}C incorporation (from ethane), which quite rapidly levels off, giving a smoother isotope distribution. All the aromatic products show this tendency.

We believe that this phenomenon is caused be a stoichiometric reaction between ethane and Ga_2O_3 on the catalyst, whereby ethane is oxidized and Ga_2O_3 is reduced to its catalytically active state. However, another possibility is that methanol is mainly used to generate a hydrocarbon pool in the catalyst during the first minutes, which would lead to an excess of ^{12}C from ethane in the products.

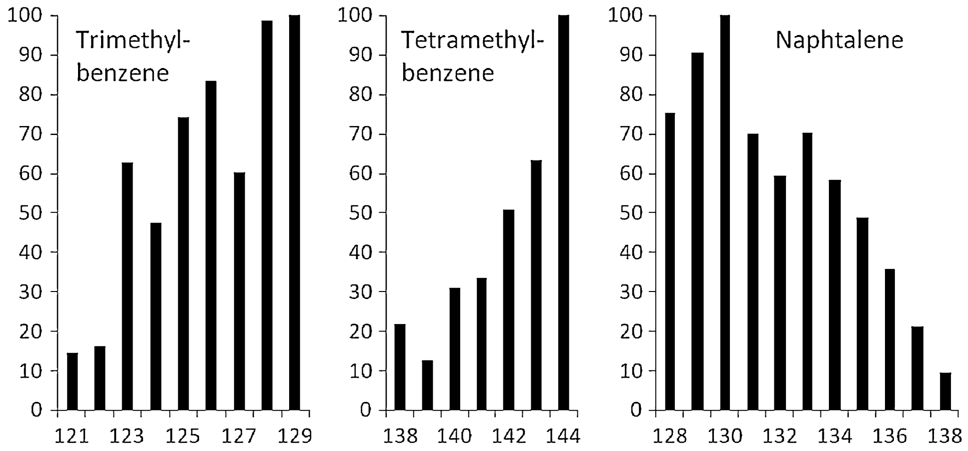
After the induction period, we see that carbon atoms from ethane and methanol are still mixed in the products. This clearly shows that we have a hydrocarbon pool mechanism, where both methanol and ethane are incorporated, leading to scrambling of isotopes in the products.

To extract information about the hydrocarbon pool in the catalysts, the zeolites are dissolved after the catalytic tests and the deposited carbon species are investigated by GC–MS. Figure 4 shows mass spectra of some hydrocarbon species generated in the catalyst in a co-conversion experiment of unlabeled ethane and ^{13}C-labeled methanol over Ga/H-ZSM-5. The fact that the isotopes are completely mixed confirms that a hydrocarbon pool, where both ethane and methanol are incorporated, is generated in the catalyst. But even though both reactants are involved in the mechanism, they may have completely different reaction pathways in the hydrocarbon pool. For instance, naphthalene has a much higher content of ^{12}C (from ethane) than both trimethylbenzene and tetramethylbenzene, indicating that they are produced via different reaction mechanisms. We have not looked further into the mechanistic details, since it is beyond the scope of this study.

4 Conclusions

The presence of methanol is not beneficial for the conversion of ethane in our experiments; the conversion of ethane actually drops when methanol is present. We believe this is due to competition for the active sites; methanol simply takes up the sites leaving ethane unreacted. The fact that the presence of methanol has a pronounced negative effect on the conversion of ethane is somewhat surprising since Choudhary et al. [15] reported a successful activation of methane in the presence of methanol using similar conditions and catalysts as in our study.

Fig. 4 Mass spectra of different carbonaceous compounds deposited on the catalyst after co-conversion of unlabeled ethane and ^{13}C-labeled methanol over Ga/H-ZSM-5 for 2 h



^{13}C-labeling studies indicate an initial activation of the catalyst where ethane reduces Ga_2O_3 to its catalytically active state. The labeling studies also clearly show that carbon atoms from ethane and methanol are mixed in the products and in the deposited carbonaceous material on the zeolite. This indicates that both ethane and methanol take part in the formation of a hydrocarbon pool in the catalyst, from where the products are formed, i.e., ethane and methanol are successfully co-converted in the sense that they are involved in the same overall reaction mechanism. However, the co-conversion does not promote the conversion of ethane.

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