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Aromatization of ethanol on Mo_2C/ZSM catalysts

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The reaction of ethanol was investigated on Mo_2C, Mo_2C/SiO_2 and Mo_2C/ZSM-5 catalysts at temperature ranging 573–973 K under atmospheric pressure. Mo_2C and Mo_2C/SiO_2 catalyzed only the decomposition of ethanol to H_2, ethylene, acetaldehyde and different hydrocarbons. The main reaction pathway on pure ZSM-5 is the dehydration reaction yielding ethylene, small amounts of hydrocarbons and aromatics. Deposition of Mo_2C on zeolite greatly enhanced the yield of benzene and toluene by catalyzing the aromatization of ethylene formed in dehydration process of ethanol.

KEY WORDS: ethanol decomposition; aromatization of ethanol; aromatization of ethylene; Mo_2C/ZSM-5 catalyst.

1. Introduction

A great effort is being nowadays made for the utilization of cheap raw materials, such as CO_2 and CH_4 to produce more valuable compounds [1]. As regards the reaction of methane recent studies revealed that the combination of Mo_2C with ZSM-5 can convert CH_4 into benzene with ~80% selectivity at 10–12% conversion [2–7], which opened a new route for its better economic use. This finding is going to have industrial application. Mitsubishi Chem. Co with the cooperation of other companies decided to construct a 250.000 t/year scale commercial plant for the MTB (methane to benzene) process [8].

Besides CO_2 and CH_4, however, ethanol is also going to gain an increased application, as it can be rather easily obtained from biomass fermentation. Beside using as fuel in automobile, it is a good candidate as a basic material to produce H_2 in fuel cells and in electric vehicles [9–11]. An alternative application is to convert ethanol into more valuable CH_x compounds. In the present work an account is given on the conversion of ethanol into aromatics, which received very little attention, yet. As a catalyst we use Mo_2C-containing ZSM-5 zeolite, which proved to be an effective material in the aromatization of methane [2–8] and various alkanes [12, 13].

It is well known that the dehydration of ethanol is catalyzed readily by various solids containing acid sites [14–17]. The complete conversion of ethanol was found over a series of zeolites above 573 K, but higher hydrocarbons occurred to a significant extent only on zeolite of high Bronsted acidity [18–24]. The formation of aromatics was also observed: their maximum content in the products was 8–12% [17–24]. Recently, Takahara *et al.* [17] found that at 453–573 K under atmospheric pressure ethanol decomposed to ethylene via diethyl ether. The catalyst activity was correlated with the number of strong Bronsted acid sites. Interestingly, the formation of aromatics was not observed or reported [17].

2. Experimental

2.1. Methods

Catalytic reaction was carried out at 1 atm of pressure in a fixed-bed, continuous flow reactor consisting of a quartz tube (8 mm id) connected to a capillary tube [5,13]. The flow rate was in general 40 mL/min, but the reaction was also studied at different space velocities. The carrier gas was Ar, which was bubbled through the ethanol at room temperature: its content was ~9.0%. Generally 0.3 g of loosely compressed catalyst sample was used. In the case of the study of ethylene, we applied the same experimental procedure. The ethylene content of the carrier gas was ~10.0%. Reaction products were analyzed with two gas chromatographs: a HP 5890 equipped with PORAPAQ Q+S packed column (reaction of ethanol) and a HP 4890 equipped with PORAPAQ Q+S and 30-m long HP-PLOT Al_2O_3 column (reaction of ethylene).

2.2. Materials

Mo_2C-containing catalysts were the same as used in the previous study [13]. Unsupported Mo_2C was prepared by the carburization of MoO_3 (products of ALFA AESAR) by C_2H_6/H_2 [25]. The oxide was heated under

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10% v/v C_2H_6/H_2 gas mixture from room temperature to 900 K at a heating rate of 0.8 K/min. Afterwards the sample was cooled down to room temperature under argon. The carbide was passivated in flowing 1% O_2/He at 300 K. The surface area of Mo_2C is 20 m^2/g. According to XRD analysis Mo_2C prepared in this was is in β form. Supported Mo_2C catalysts have been made in the similar ways by the carburization of MoO_3-containing supports with C_2H_6/H_2 gas mixture. The MoO_3/support samples were prepared by impregnating the support with a basic solution of ammonium heptamolybdate to yield 2 wt% of MoO_3. The suspension was dried and calcined at 863 K for 5 h. The following materials were used as support: ZSM-5 (Zeolyst Intern. Ltd.) with SiO_2/Al_2O_3 ratio at 80, BET area: 425 m^2/g. SiO_2 (Aerosil, 380 m^2/g). In order to remove the excess carbon deposited on the Mo_2C during the preparation, the catalyst has been reduced before the catalytic measurements in situ at 873 K in H_2 stream for 60 min. The gases used were of commercial purity (Linde). All the catalyst samples have been characterized before by XPS. The binding energy for Mo($3d_{5/2}$) showed some slight variation with different samples, but it fell in the range 227.7–228.2 eV, and for C(ls) 283.8 eV. These values are consistent with those attributed to Mo_2C [5,26].

3. Results and discussion

Mo_2C prepared by C_2H_6/H_2 gas mixture exhibited a high activity towards ethanol. The decomposition of ethanol was observed even at 573 K. The main product was ethylene with a selectivity of 65–55% at 773–873 K. Interestingly, acetaldehyde was also formed at this temperature range with a selectivity of 10–15%. Other compounds formed were ethane, methane, propene and butenes. Aromatics were not identified.

The conversion of ethanol increased when Mo_2C was deposited on silica. Almost 75–85% conversion was attained at 773 K. The main product was again ethylene with a selectivity of 40–65% at 773–973 K followed by ethane, methane, propene and butenes. Aromatics were produced only in minor amounts, their total selectivity remained below 1.0–1.5%.

More attractive results were obtained when Mo_2C was combined with zeolites. We choose a ZSM-5 with SiO_2/Al_2O_3 ratio of 80. The reaction of ethanol on pure ZSM-5(80) occurred at very low temperature, 423–473 K, yielding mainly diethyl ether and ethylene. The former one disappeared above 573–623 K, while the selectivity of ethylene increased with the temperature from ~55% (573 K) to ~83% (873 K). The formation of aromatics, toluene, benzene, xylene and C_9, was observed from 523 K. The total selectivity of aromatics in the temperature range of 573–873 K remained at low level: the highest value was 12–13%. The same products were found on 2%Mo_2C/ZSM-5(80) catalyst, but with different distribution. Although the conversion of ethanol was only slightly enhanced by Mo_2C, the selectivities for aromatics have been increased by 60–80%. The optimum temperature of the formation of aromatics appeared to be 773–873 K. At higher temperatures the capability of the catalyst to produce aromatics gradually decayed.

Figure 1 shows the effect of space velocity on the selectivity of various products on pure and Mo_2C-containing ZSM-5(80) at 873 K. At this temperature the conversion of ethanol approached 100%. The general feature for both catalysts is that the selectivity of aromatic compounds are the highest at the lowest flow rate. Their selectivity gradually decreased with the rise of space velocity together with that of other products. An exception is ethylene, the dominant product of the reaction, the selectivity of which increased with the flow rate of ethanol + Ar gas mixture. Note that the formation of diethyl ether and acetaldehyde has not been identified on either samples. An important finding is that the selectivity of the total aromatics was always much higher on Mo_2C/ZSM-5 (80) compared to pure zeolite.

As a large amount of ethylene was found in the products, in separate experiments we examined its reaction on the catalyst samples used in this work. Results obtained are shown in figure 2. Ethylene is aromatized readily on ZSM-5(80) yielding benzene, toluene and xylene with decreasing selectivities. Whereas their total selectivity was relatively low, ~15%, on pure ZSM-5 (80) at 773 K, it increased to 28% at 873 K and to 56% at 973 K. Other main products were propene and 1-butene. Deposition of Mo_2C on this zeolite exhibited relatively little promoting effect on the conversion, but influenced the product distribution (figure 2b). On 2%Mo_2C/ZSM-5(80) catalyst the above selectivity values increased to 29%, 59% and 77%, respectively. The enhanced formation of aromatics occurred at the expense of alkanes and alkenes. Mo_2C/ZSM-5 was found to be a rather stable catalyst at 773–873 K, but the deactivation occurred rapidly at 973 K. From the study of the effect of the space velocity we obtained that the selectivities of the aromatics decreased, while those of other major products, propene, butene and pentene, increased with the rise of the flow rate (figure 3).

In the explanation of the promoting effect of Mo_2C we should take into account that on acidic zeolite, such as ZSM-5, lower alkenes oligomerize through a carbenium-ion mechanism over protonic sites followed by isomerization and decomposition to produce a variety of lower alkanes [27]. In addition to this complex reaction sequence, the presence of Mo_2C opens a new route for the activation of ethylene. It acts as dehydrogenation centers for ethylene resulting in different products, which are converted into aromatics. Data obtained from the variation of the residence time suggest that the formation of aromatics from ethylene occurs in secondary processes.

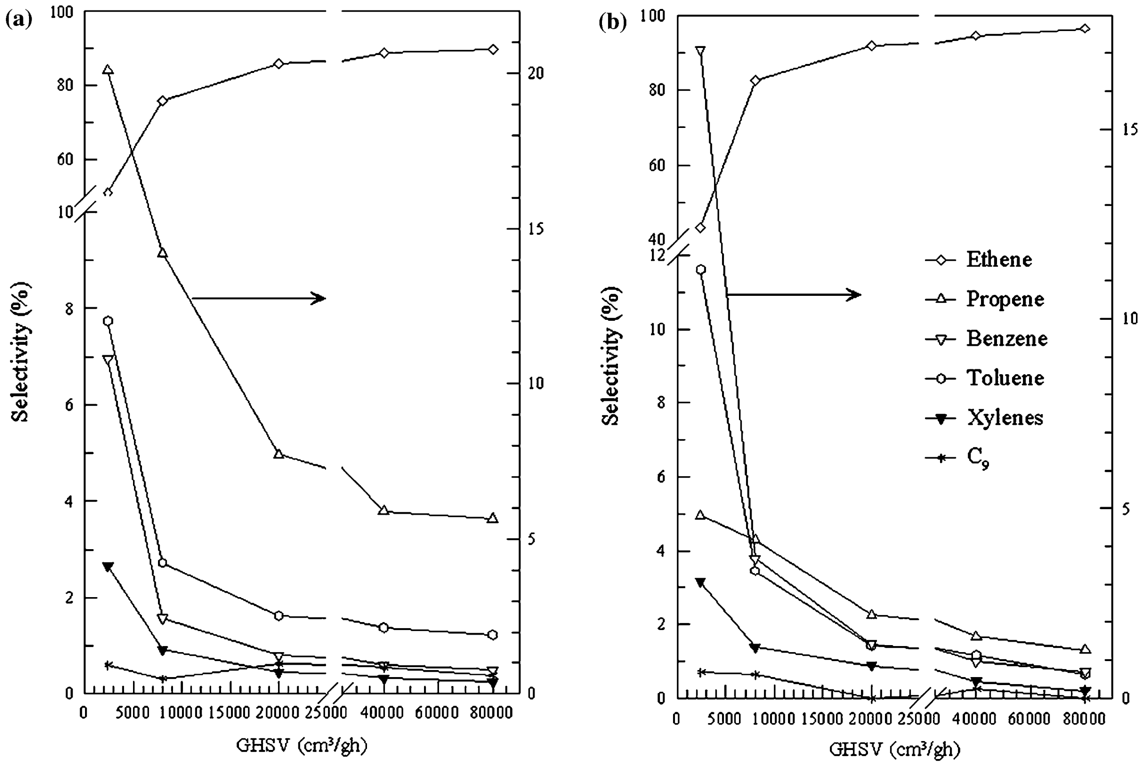

Figure 1. Effects of flow rate on the selectivity of various products formed in the reaction of ethanol at 873 K. (a) ZSM-5 (80); (b) 2% Mo_2C/ZSM-5 (80).

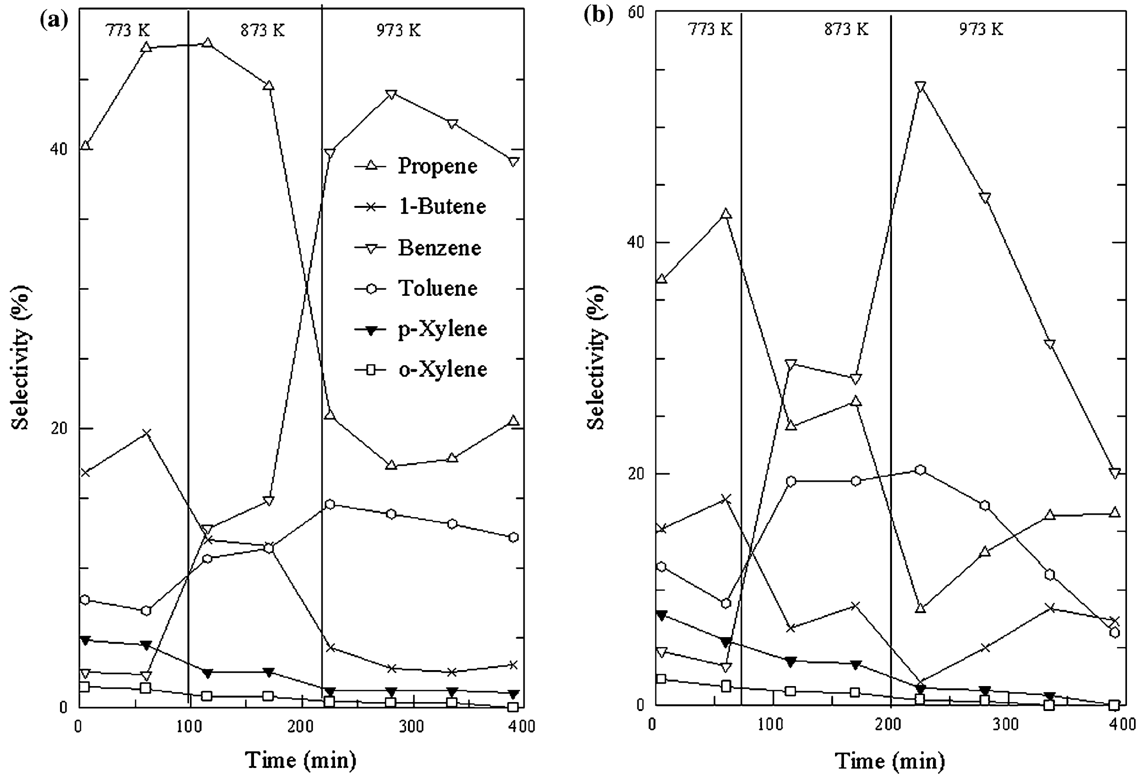

Figure 2. Reaction of ethylene over ZSM-5 (80) (a) and 2% Mo_2C/ZSM-5 (80) (b) at different temperatures.

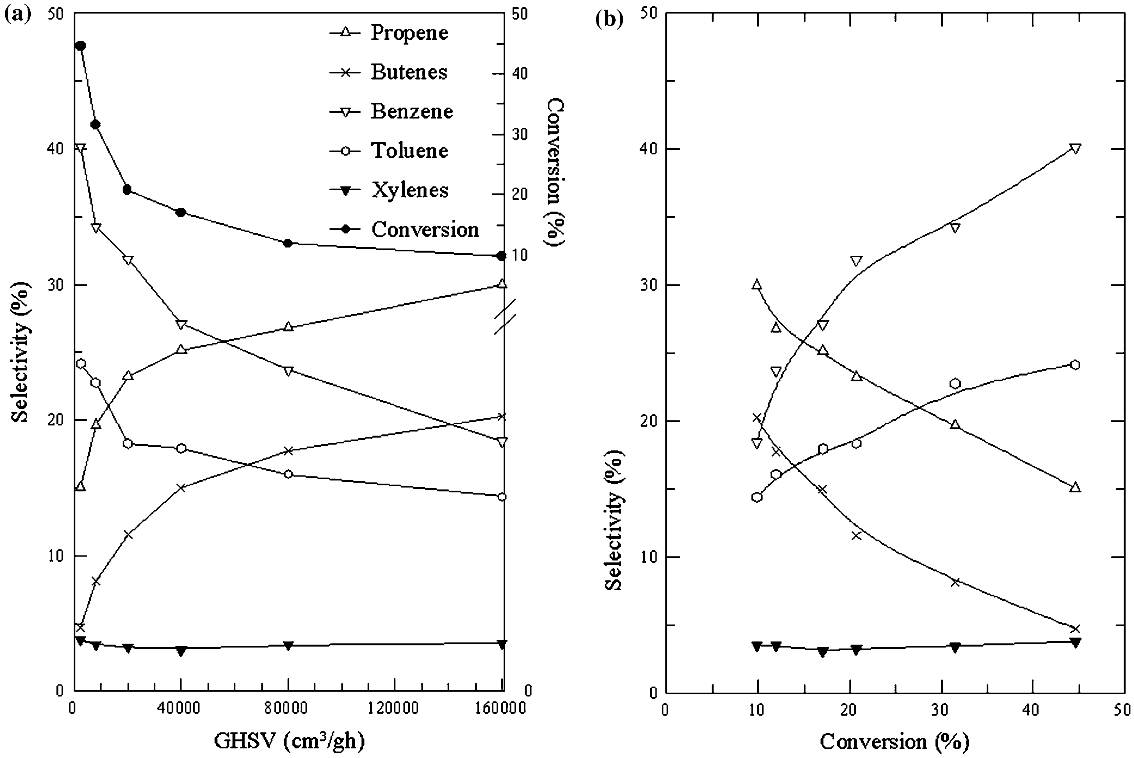

Figure 3. Effects of flow rate on the selectivity of various products formed in the reaction of ethylene at 873 K. (a) ZSM-5 (80); (b) 2% Mo_2C/ZSM-5 (80).

As the ZSM-5 (80) is an effective catalyst for the dehydration of ethanol and the presence of Mo_2C can markedly promotes the aromatization of ethylene, we examined whether we could enhance the formation of aromatics by using two beds of catalyst. This approach was found to be very effective in the case of the aromatization of ethane over Re/ZSM-5 catalyst [28]. In the first bed we put pure ZSM-5 (80) and in the second bed 2% Mo_2C/ZSM-5 (80) was placed. The two beds were separated by glass wool of 1.5–2.0 mm thick. Results obtained are given in table 1. As was expected, the selectivity of all aromatics, was enhanced at the expense of thylene formation. The yield of aromatics at 773 K increased from 13,1% to 24,8 %.

As ethylene is aromatized readily on Mo_2C/ZSM-5(80), an attempt was made to find out why the yield of aromatics is not much higher in the reaction of ethanol. One of the probable reasons was the inhibiting and poisoning effect of water formed in the primary process of ethanol. This idea was proved by experiments. While the addition of a small amount of water to ethylene (H_2O/C_2H_4 ratio ~0.3) influenced only little the course of the reaction on Mo_2C/ZSM-5(80), a larger amount of water, (H_2O/C_2H_4 ratio ~1.4), however, resulted in a

Table 1
Characteristic data for the reaction of ethanol and ethylene on diferent catalysts

T [K]		Water %	Conv. %	Total selectivity of aromatics %	Yield of aromatics
Reaction of ethanol					
773	H/ZSM-5 (80)		~ 100	13.1	13.1
773	H/ZSM-5 (80) + 2% Mo_2C/ZSM-5 (80)*		~ 100	24.8	24.8
Reaction of ethylene					
773	2% Mo_2C/ZSM-5 (80)	0	36.9	19.3	7.1
773	2% Mo_2C/ZSM-5 (80)	3	30.2	21.2	6.4
773	2% Mo_2C/ZSM-5 (80)	14	30.7	21.0	6.4
873	2% Mo_2C/ZSM-5 (80)	0	41.0	52.4	21.5
873	2% Mo_2C/ZSM-5 (80)	3	20.2	45.9	9.3
873	2% Mo_2C/ZSM-5 (80)	14	17.1	44.8	7.7

decay in the conversion and also in the selectivity of aromatics. Some characteristic data are presented in table 1.

Experiments are in progress to improve further the yield of aromatics by variation of the experimental conditions, the composition of ZSM-5 and by using more effective promoters.

4. Conclusions

(i) Mo_2C and Mo_2C/SiO_2 catalyzed only the decomposition of ethanol mainly to hydrogen, ethylene and acetaldehyde.
(ii) Deposition of Mo_2C on ZSM-5 markedly promoted the formation of aromatics from ethanol.
(iii) This feature of Mo_2C was attributed to its effect on the aromatization of ethylene formed in the dehydration of ethanol occurring on ZSM-5.

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