

Influence of Zn- and Ga-doping on the conversion of ethanol to hydrocarbons over ZSM-5

S.K. Saha and S. Sivasanker

National Chemical Laboratory, Pune 411 008, India

Received 17 March 1992; accepted 2 June 1992

The influence of incorporating Zn and Ga in ZSM-5 on the catalytic transformation of ethanol into hydrocarbons has been investigated. Under the conditions of this study, considerable amount of hydrocarbons boiling above 423 K are produced over the catalysts. The incorporation of Zn and Ga in ZSM-5 increases its life considerably apart from increasing the yield of the liquid products. Further, the Zn- and Ga-catalysts produce more aromatics and less olefins.

Keywords: Alcohol to hydrocarbons; Ga-ZSM-5; Zn-ZSM-5; ethanol transformation

1. Introduction

Processes for the conversion of methanol to olefins and fuels over ZSM-5 catalysts are well established [1–4]. Methanol is itself obtained from fossil fuels like petroleum, natural gas or coal. The transformation of ethanol, which can be produced from a renewable source like biomass into hydrocarbons is potentially of great importance to countries like Brazil and India which have a large agricultural base. In these countries, ethanol is generally produced by the fermentation of molasses, a by-product of their huge sugar industry. A considerable amount of information on the conversion of ethyl alcohol to hydrocarbons over H-ZSM-5 is available in the literature [5–9].

Earlier studies [8,9] have revealed that the composition of the product is determined by the aluminium content ($\text{SiO}_2/\text{Al}_2\text{O}_3$) of ZSM-5, higher aluminium contents favouring the formation of heavier products. We have carried out the conversion of industrial ethanol over H-ZSM-5 and ZSM-5 loaded with Zn and Ga ions. We find that the incorporation of Zn and Ga also increases the yield of gasoline and kerosene range hydrocarbons (heavier products), besides increasing the life of the catalyst. Aromatic contents of the products are also more in the case of Zn and Ga.

2. Experimental

ZSM-5 was prepared as per published procedure [10]. The as-synthesised sample was washed in water, calcined at 773 K in dry air for 6 h, and converted into the NH_4 -form by exchange with an ammonium nitrate solution. The NH_4 -form was then calcined in air (773 K; 4 h) to yield H-ZSM-5. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the zeolite was 82, and it had an average crystallite size of about 0.5 μm . The zeolite powder (75 g) was then blended with alumina hydrate powder (100 g, Catapal-B, Vista Chemicals, USA) and an aqueous solution of acetic acid (3 wt%), extruded in a hand press, dried and calcined at 773 K for 6 h. The extrudates were 1/16 inch in diameter and consisted of a 50:50 (wt%) blend of zeolite and γ -alumina. The zeolite and mesopore (non-zeolite) areas of the extrudates obtained by argon adsorption [11] (Omnisorp CX 100; Coulter-Omicron, USA) were 214 and 127 m^2/g , respectively. The corresponding areas for the parent ZSM-5 were 413 and 7 m^2/g . The values indicate a zeolite content of about 52 wt% in the catalyst. Similarly XRD-intensities also revealed a zeolite content of about 50 wt% in the final catalysts. These results suggest the absence of significant pore blockage and zeolite loss during the preparation of the extrudates. Also, as a dilute solution of acetic acid (weak acid) was used for peptization, changes in the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the zeolite are unlikely.

The extrudates were soaked in the required amount of zinc or gallium nitrate solutions, evaporated to dryness and calcined at 773 K for 6 h to obtain the Zn- or Ga-doped catalysts. The catalysts contained 3 wt% of Zn or Ga as oxides.

Ethanol conversion was carried out in a high pressure fixed bed, continuous flow reactor (Twin Reactor, Type OL-105/02 supplied by Metrimpex, Hungary) in a single pass mode. Industrial ethanol (88% v/v, alcohol/water; rectified spirits) was used in the study. The analysis of the gaseous products was carried out using a Porasil-C column. The liquid products were analysed by a gas-chromatographic simulated distillation technique (Hewlett Packard, 18900 C option 840) to obtain the distillation pattern. The gasoline fraction was analysed using a HP 1 capillary column (cross-linked methyl silicone gum, 50 m \times 0.5 mm).

3. Results and discussion

In the conversion of alcohol to hydrocarbons, the loss in the yield of the liquid products with time is a measure of the deactivation of the catalyst. The addition of Zn and Ga lowers (fig. 1) the tendency to deactivate. The liquid yield (C_{5+}) remains constant for much longer periods in the case of Zn- and Ga-containing samples. Further, the rate of loss in liquid yield is also much slower for Zn- and Ga-ZSM-5. The increase in yield of ethylene with duration of the run is found to be more rapid in the case of H-ZSM-5 than in the case of the Zn- and Ga-doped catalysts. Generally, the increase in concentration of the primary

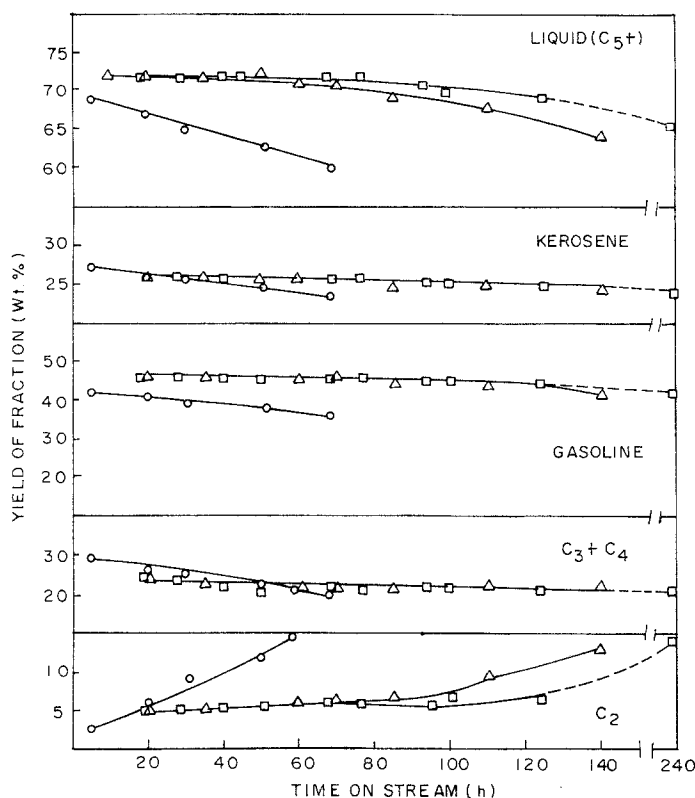
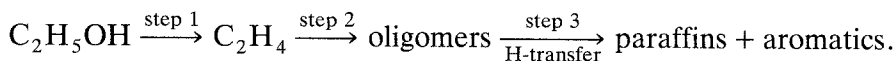


Fig. 1. Product distribution over H-, Zn- and Ga-ZSM-5. (○) H-ZSM-5, (△) Zn-ZSM-5, (□) Ga-ZSM-5. Gasoline: C_5 423 K fraction; kerosene: 423–573 K fraction. Conditions: $T = 633$ K; $p = 10$ atm; WHSV 1 h^{-1} .

product, viz. ethylene, in the product mixture is also related to the deactivation of the catalyst, the more deactivated catalyst producing more ethylene. The sequence of reactions taking place on the catalyst surface is



Assuming an activity decay similar to that predicted by the Voorhies equation [12,13], $k = At^{-n}$, the deactivation coefficient (n) for the loss of C_{5+} yield has been calculated for the three catalysts. The values are 2.04×10^{-3} , 1.07×10^{-3} and 0.45×10^{-3} , for H-ZSM-5, Zn-ZSM-5 and Ga-ZSM-5, respectively. The Ga-doped catalyst deactivates the least.

A more detailed break-up of the gaseous components is presented in fig. 2. The yield of methane is larger over H-ZSM-5 than over the other two catalysts and the olefin content (mainly ethylene) of the gaseous fraction increases more rapidly with duration of the run in the case of H-ZSM-5 vis-a-vis the others.

Zn and Ga containing ZSM-5 catalysts have been found to be useful in the aromatisation of light hydrocarbons [14]. The role of these promoters in increas-

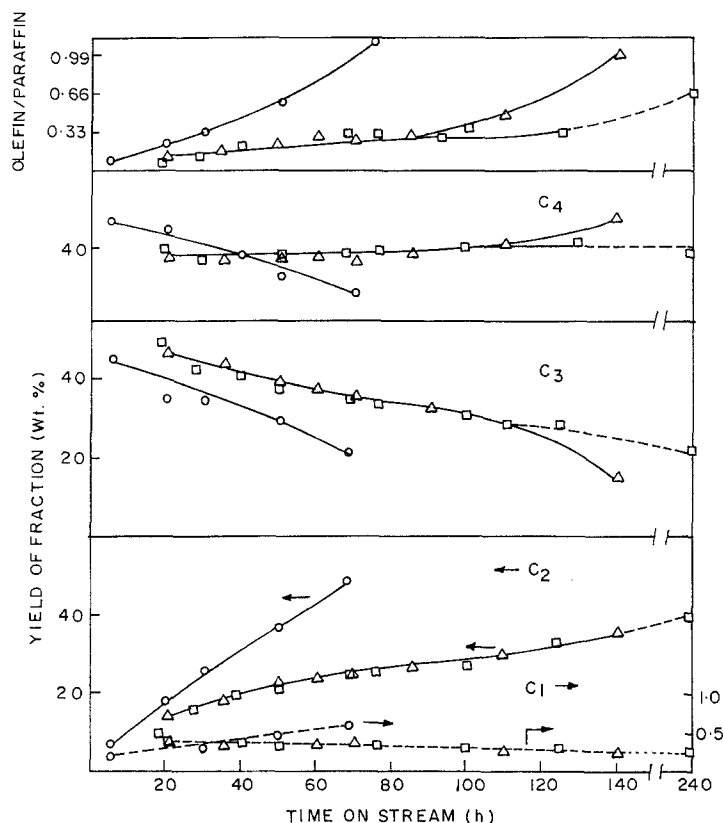


Fig. 2. Break-up of gaseous products and olefin/paraffin ratio of the gaseous fraction obtained over H-, Zn- and Ga-ZSM-5. (○) H-ZSM-5, (△) Zn-ZSM-5, (□) Ga-ZSM-5. Conditions: $T = 633$ K; $p = 10$ atm; WHSV 1 h^{-1} .

Table 1
Influence of Zn and Ga incorporation on C_6 - C_8 aromatics yield^a

Aromatic compound	Yield (wt%)		
	H-ZSM-5	Zn-ZSM-5	Ga-ZSM-5
benzene	1.12	1.47	1.10
toluene	7.54	11.50	8.92
<i>m</i> -xylene	6.41	7.55	7.65
<i>p</i> -xylene	2.62	3.62	3.17
<i>o</i> -xylene	2.69	2.64	3.02
ethyl benzene	2.84	3.77	3.67
total	23.22	30.55	27.53
bromine number (g/100 g)	13.6	9.0	12.6

^a In C_5 423 K fraction: detailed break-up of the paraffins and olefins has not been possible due to difficulty in identification of all the compounds. However, bromine number values (indicating olefinic content) are reported.

ing the aromatisation activity of ZSM-5 is still under debate [15]. The larger amount of saturates in the gaseous fraction in the case of Zn and Ga containing catalysts suggests that these catalysts have larger H-transfer abilities [16] than H-ZSM-5. Again, it is observed (table 1) that aromatics production is also more over the Zn and Ga catalysts than over H-ZSM-5. Further, the bromine numbers (measure of the total olefin content) are also lower on the Zn and Ga catalysts. The bromine number [17] values for the C_{5+} fractions were 13.6, 9.0 and 12.6, respectively, for the H-, Zn- and Ga-ZSM-5 samples. These results confirm that H-transfer reactions increase when Zn and Ga are incorporated in H-ZSM-5. It is possible that the greater stability of the Zn and Ga forms is also related to this property; the greater H-transfer ability of these catalysts might be helping in desorbing the strongly adsorbed olefins as saturates and aromatics.

4. Conclusions

In the transformation of ethanol to hydrocarbons, use of a ZSM-5 ($SiO_2/Al_2O_3 = 82$): Al_2O_3 (50:50 wt%) catalyst produces significant amounts of hydrocarbons in the gasoline and kerosene range (> 423 K). Incorporation of Zn and Ga not only increases the yield of the liquid products, but also increases the life of the catalyst. Further, the liquid products are more aromatic in nature in the case of the Zn and Ga containing catalysts.

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