Aromatization of propane over Ga/H-ZSM-5: An explanation of the synergy observed between Ga^{3+} and H^+

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The aromatization of propane is investigated for Ga_2O_3, H-ZSM-5 and Ga_2O_3/H-ZSM-5 catalysts, and the results are discussed for a series of ZSM-5 catalysts containing varying SiO_2/Al_2O_3 ratios. It is apparent that on addition of a gallium phase to H-ZSM-5, the yield of methane is significantly decreased. These results are discussed with respect to the mechanism of formation of the initial reaction product from propane. It is proposed that the synergy observed between the gallium compound and the zeolite can be explained in terms of a mechanism in which the role of the gallium phase is to induce C-H bond polarization in the propane, which leads to attack via the Bronsted acid sites of the zeolite, which leads to initial C-H bond cleavage occurring.

Keywords: Propane aromatization; zeolite H-ZSM-5

1. Introduction

In recent years the utilization of light alkanes has received considerable research attention. One potential process is the BP Cyclar process in which propane and butane are aromatized to form benzene, toluene and xylene [1]. Of the catalysts investigated to date, the gallium promoted pentasil zeolite H-ZSM-5 gives the best results [2]. Consequently this catalyst system, as well as alternative zeolite systems modified by gallium, has been studied, particularly with respect to the elucidation of the mechanism of activation of propane. A number of studies [3,4] have shown that the activation of propane involves a synergy between the gallium phase and the Bronsted acid sites of the zeolite. In particular, studies by Merriaudeau and Naccache [3] and Bayense et al. [4] have led to the proposal that the gallium phase acts as a hydride acceptor in the initial activation of propane to form a $C_3H_7^+$ carbenium ion, which subsequently reacts with the zeolite. This communication examines the validity of such a proposal and aims to probe further the origin of this synergistic effect.

2. Experimental

H-ZSM-5 zeolite was prepared by the method of Howden [5] with SiO_2/Al_2O_3 ratios of 35, 185 and 280. Gallium was added to H-ZSM-5 either by an ion exchange procedure using aqueous nitrate solution (0.05 M, 100 ° C for 24 h, zeolite dried at 100 ° C), or by physically mixing βGa_2O_3 (Aldrich 99.99 + %) with H-ZSM-5 (Ga_5O : H-ZSM-5 = 1 : 19). Catalytic reactions were carried out using a stainless steel microreactor, previously described [6].

3. Results

H-ZSM-5 and gallium modified H-ZSM-5 catalysts were investigated for the propane aromatization reaction and the results are given in table 1. It is apparent that as the SiO_2/Al_2O_3 ratio of H-ZSM-5 increases from 35 to 280, both the conversion of propane and the yield of aromatics decreases. Such effects can readily be explained as a consequence of the reduction in the concentration of acid sites of H-ZSM-5 as the SiO_2/Al_2O_3 ratio increases, since acid sites are essential for both the initial activation of propane, as well as the aromatization of reaction intermediates [2]. The addition of gallium either by ion exchange or by physically mixing Ga_2O_3 with H-ZSM-5 leads to an enhancement in both propane conversion and yield of aromatics for all the H-ZSM-5 samples. However, the effect of gallium addition is more marked for the samples with high SiO_2/Al_2O_3 ratios; eg. addition of 5% Ga_2O_3 to H-ZSM-5

Table 1

Sample [a]	Ga%	Conv/%	Product yield/$g \cdot min^{-1}$ [b]	
			CH_4	BTX
Ga_2O_3 [c]	74.4	13.5	3.14×10^{-4}	5.31×10^{-5}
H-ZSM-5 (35)	0	80.8	7.19×10^{-3}	13.79×10^{-3}
Ga_2O_3/H-ZSM-5 (35)	3.7	83.6	5.90×10^{-3}	17.08×10^{-3}
Ga-ZSM-5 (35)	3.4	84.6	4.88×10^{-3}	20.20×10^{-3}
H-ZSM-5 (185)	0	19.6	1.89×10^{-3}	7.98×10^{-5}
Ga-ZSM-5 (185)	2.6	41.5	1.71×10^{-3}	7.23×10^{-3}
H-ZSM-5 (280)	0	6.6	5.67×10^{-4}	0
Ga_2O_3/H-ZSM-5 (280)	3.7	8.8	3.15×10^{-4}	15.17×10^{-5}
Ga-ZSM-5 (280)	2.1	13.7	4.81×10^{-4}	7.10×10^{-4}

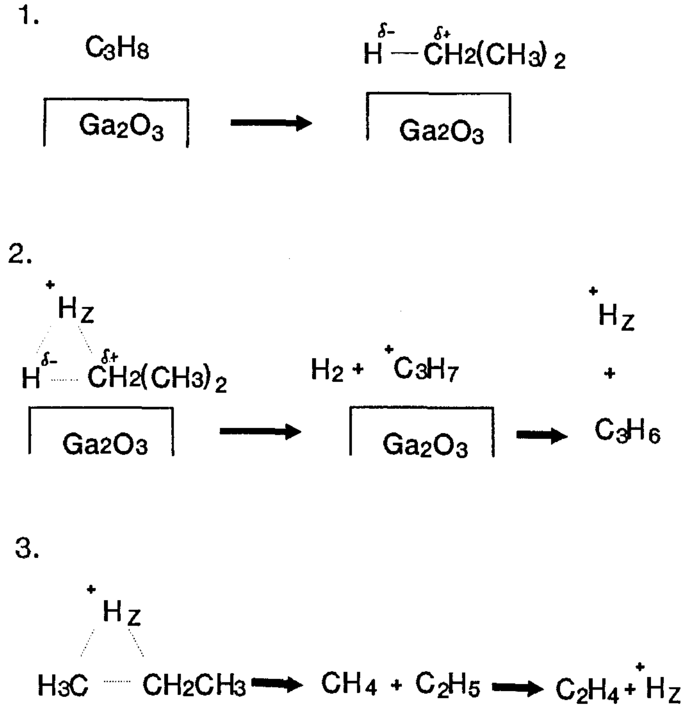
[a] The number in brackets indicates the SiO_2/Al_2O_3 ratio.
[b] Reaction conditions: catalyst 0.5 g, propane WHSV = 4.7 h^{-1}, 600 ° C.
[c] Pure gallium oxide tested under identical conditions to H-ZSM-5.

($SiO_2/Al_2O_3 = 35$) gives a 35% increase in propane conversion, whereas addition of the same amount of Ga_2O_3 to H-ZSM-5 ($SiO_2/Al_2O_3 = 280$) leads to a 33% in propane conversion. It is apparent that the addition of gallium to the zeolite decreases the yield of methane for all the zeolite samples. The results for pure Ga_2O_3 are also given under comparable reaction conditions to demonstrate the synergistic effect that exists in this catalyst system between the gallium phase and the zeolite, as has been noted previously [6].

4. Discussion

The proposals of Merriaudeau and Naccache [3] and Bayense [4] to explain the synergistic effect are in agreement, in that the role of the gallium phase is to act as a hydride acceptor from propane to form a carbenium ion $C_3H_7^+$. It is then proposed that the carbenium ion so formed reacts with the zeolite component, either with the Bronsted acid sites or the conjugate basic sites to form propene, the primary reaction product. This model of the catalytic system essentially views the gallium and zeolite components as separate entities and that transfer of the intermediate carbenium ion is required between the two phases. In support of this model is the observation that gallium ion exchange of zeolite samples essentially leads to the formation of gallium oxide as a separate phase, since the hydrated gallium cation is too large to enter the internal microporous structure of the crystallite of H-ZSM-5 [7]. However, if such a model is correct, then all the Bronsted acid sites within the zeolite are available for interaction with propane that has not been activated by the gallium phase. Since propane is always present in excess, such a model predicts that the rate of propane cracking to methane and ethene, via $C_3H_9^+$ carbonium ion formation, should remain approximately constant for both H-ZSM-5 and gallium modified H-ZSM-5, particularly if the gallium is added as Ga_2O_3 by the physical mixing method. However, the results of our investigation demonstrate that the methane yield is significantly decreased on addition of gallium to H-ZSM-5 for all SiO_2/Al_2O_3 ratios investigated. This suggests that when the gallium compound is present the Bronsted acid cracking of propane is suppressed and such an observation is not consistent with the proposals of Merriaudeau and Naccache [3] or Bayense et al. [4].

In addition, it is apparent for the data presented in table 1 that the relative enhancement on propane activation and aromatics formation is most pronounced for the sample with the highest SiO_2/Al_2O_3 ratio. For the samples prepared by the physical mixing method, the number of Lewis acid sites present in the catalyst system, as discussed by Bayense et al. [4], remains constant. Yet the promotional effect of gallium is enhanced for the catalyst system with the decreased Bronsted acid site concentration. This observation is also not consistent with the proposals of Bayense et al. [4] or Merriaudeau and Naccache [3],



$^{+}H_Z$ denotes proton associated with the zeolite

Fig. 1. Proposed mechanism of propane activation on Ga_2O_3/H-ZSM-5.

since in their proposals the concentration of Bronsted acid sites is also of critical importance. For example, in the proposal of Merriaudeau and Naccache, the loss of H^+ from $C_3H_7^+$ is considered to occur on the zeolite.

Furthermore, it is proposed [3] that the rate limiting step on propene formation is the loss of H^+ from $C_3H_7^+$. It is unlikely that such a step should be slow in comparision to the initial hydride abstraction from the stable C_3H_8 molecule required to form the $C_3H_7^+$ carbenium ion. It is more likely that the rate limiting step involves the initial C–H bond cleavage and we propose that the zeolite Bronsted acid site is directly involved in this process.

We propose that the mechanism of propane activation on gallium promoted H-ZSM-5 is as follows. Infra-red studies have shown [7] that C–H bound polarization can occur on Ga_2O_3. Hence, C–H bond polarization occurs in C_3H_8 as the initial step in the activation (step 1, fig. 1). Subsequently, C–H bond cleavage is facilitated by the interaction of the polarised C–H bond with the Bronsted acid site of the zeolite phase (step 2, fig. 1), in a reaction that is analogous to that considered to occur in propane cracking over zeolite catalysts

[8], (step 3, fig. 1). The role of the gallium phase is therefore to induce C–H bond polarization in propane, which makes it more susceptible to attack by Bronsted acid sites of the zeolite. The role of the zeolite is to increase the rate of initial C–H bond cleavage and thereby increasing the conversion of propane. In this way the reaction leading to C–C bond cleavage of propane is decreased and hence the yield of methane is decreased on addition of gallium to H-ZSM-5. In this mechanistic proposal it is envisaged that the gallium and zeolite phases act in concert, and that the active site for propene formation is at the interface between the gallium phase and the zeolite.

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