Comments on: Evidence for the reversible formation of a catalytic active site for propane aromatization for Ga_2O_3 / H- ZSM-5. A response

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In our earlier paper [1], which has been commented on by Mériaudeau and Naccache [2], we described the experimental data obtained for the reaction of physical mixtures of Ga_2O_3 and H-ZSM-5 for a short reaction time of 5 min. The aim of these experiments was to simplify a complex catalyst system to demonstrate whether simple contact synergy can be used to explain the nature of the active site. We were aware that under specific reaction conditions Ga_2O_3 could be reduced and transported to the micropores of the H-ZSM-5 zeolite and indeed numerous previous studies have shown this effect [3]. However, the conditions we selected were chosen to minimise this effect, as far as possible, to investigate the initial activity of Ga_2O_3/H-ZSM-5 catalysts. We concluded that the results could be interpreted in terms of an active site being created at the interface between the Ga_2O_3 and the H-ZSM-5 and that no induction period was necessary to observe this effect [1]. In a subsequent paper we have extended and further shown this effect [4]. The data presented by Mériaudeau and Naccache for experiments carried out for a duration of 5 min would appear, on initial inspection, to be at variance with our findings and they deserve to be commented on further.

In a typical experiment in our previous studies [1] the Ga_2O_3/H-ZSM-5 catalyst was preheated to reaction temperature (600°C) in dry N_2. Once the reaction temperature was reached the dry N_2 was switched to the required reaction feedstock (either propane/H_2 or propane/N_2). Sampling of the effluent gases indicated that at least 2 min were required from the time of the switch in the feedstock for the analysis of the reactor effluent to be representative. This delay was due to the dead volume within the reactor. For this reason we adopted 5 min after the switch in feedstocks as being representative of the initial catalytic performance. However, it should be noted that there was no appreciable difference in the catalytic performance between analysis after 2 or 5 min time on line.

The experiments of Mériaudeau and Naccache have focussed on the nature of possible structural changes that could occur in the catalyst during this initial 5 min exposure to the reaction mixture and in particular that the structure could be changed by migration of gallium oxide into the micropores. It is well known that hydrogen treatment of Ga_2O_3/H-ZSM-5 modifies the nature and the dispersion of the gallium oxide and it is therefore important to consider whether this could have occurred under our reaction conditions during this timescale. In this respect, in both our experiments and those of Mériaudeau and Naccache [2] the sample pretreatment and preparation are critical factors and on inspection it is apparent that the conditions used by Mériaudeau and Naccache are considerably different from the conditions used by us in three important ways. First, the physical mixture prepared by Mériaudeau and Naccache is an intimate mixture of the two solids made by finely grinding Ga_2O_3 and H-ZSM-5 in an agate mortar for 5 min. However, we used a mixture of Ga_2O_3 powder and H-ZSM-5 pellets prepared by gently mixing the two component parts and this will give a much poorer distribution of the Ga_2O_3. The effect of the grinding used by Mériaudeau and Naccache ensures that an intimate mixture of the two components is achieved and this will aid transfer of the Ga_2O_3 in any subsequent treatment of the catalyst. Second, the sample used by Mériaudeau and Naccache has been calcined before reaction, a procedure not used in our experiments. Third, the most significant difference, however, is that, although Mériaudeau and Naccache treat their sample for 5 min, they use a much higher molar ratio of reactants/Ga_2O_3 during this treatment. In our experiments we used 500 mg catalyst (10% Ga_2O_3/H-ZSM-5) and 10 ml/min propane at 600°C [1]. After the initial 5 min treatment period the molar ratio of total propane fed/$Ga_2O_3 = 4.03$ and this are two to three orders of magnitude lower than in the experiments of Mériaudeau and Naccache [2]. For example in their experiment using treatment C they use 20 mg catalyst (10% Ga_2O_3/H-ZSM-5) and 83 ml/min propane at 600°C which results after 5 min treatment in the molar ratio of total propane fed/$Ga_2O_3 = 8.75 \times 10^2$.

It is therefore clear that the experimental conditions used by Mériaudeau and Naccache do not replicate our conditions since they exposed an intimately ground catalyst sample to ca. 200 times more reagents. Since our experiments only lasted in total for 185 min the exposure of our catalyst to the reactants during the entire experiment will have been less than one tenth that used by Mériaudeau and Naccache in the initial 5 min treatment.

It is clear from the results presented by Mériaudeau and Naccache [2] that exposure of Ga_2O_3/H-ZSM-5 to massive doses of propane and hydrogen will cause transfer of the gallium oxide into the micropores of the zeolite. We agree with this and it has also been shown in a number of previous studies [3], but the conditions of our experiments were designed to minimise this effect. We do indicate that after 185 min reaction some of the Ga_2O_3 was transferred but this was only a minor amount. However, we contend that our experimental conditions are such that after 5 min the exposure of the catalyst to propane and hydrogen was minimal and the sample can be considered to be representative of a fresh catalyst.

We therefore conclude that the experimental conditions of Mériaudeau and Naccache [2] cause the mobility of gallium oxide and hence such conditions and sample preparation methods should be avoided in studies of this type. We conclude that the initial results obtained in our studies do indicate that a catalytic site can be formed by the simple mixing of Ga_2O_3 with H-ZSM-5 which does not require the sample to be further modified. In this respect this active site can be considered to be at the junction between Ga_2O_3/H-ZSM-5. As the sample is exposed to the reaction conditions the Ga_2O_3 will be mobilised but this effect will only increase the number of interactions (or junctions) between the gallium oxide and the zeolite. In addition, we noted in our paper [1] that the inhibitory effect of cofed hydrogen was the effect on the rate of hydrogen desorption, as noted by Iglesia and Baumgartner [5], but have used this as a means of probing the reaction mechanism and have recently extended this in a subsequent paper [4].

References

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