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COMMENT

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

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In a recent article, Buckles and Hutchings [1] have stated that new highly active sites for propane aromatization are formed on mechanical mixtures of gallium oxide and H-ZSM-5 zeolite. They concluded that on mechanical mixtures of gallium oxide and H-ZSM-5 zeolite, active sites are created at the interface of the two solids and that "there is no induction period during which the active sites are established".

By contrast, there are examples in the literature [2] which show that the aromatic yield increases following the treatment at high temperature indicating that new active sites are generated upon H_2 treatment of mixed Ga_2O_3–H-ZSM-5. We believe that, according to the experimental conditions used in ref. [1] (high temperature, high conversion), the H_2 generated during the propane transformation within the five first minutes allowed reduction and migration of gallium species as proposed earlier. To substantiate our claim the following experiments were conducted:

Mechanical mixture of Ga_2O_3 (Aldrich) with H-ZSM-5 (Si/Al = 15) was prepared by grinding the two powders (100 mg Ga_2O_3 + 1 g H-ZSM-5) in an agathe mortar for 5 min. The mixed powder was transferred in a microreactor to perform treatments and reaction with propane. As a general rule, the catalyst weight was chosen in the range of 10–20 mg and the flow of reactants adjusted between 2 and 5 ℓ/h in order to have low conversion. In all cases it has been checked that the reaction rate is independent of the conversion. Reactant and products were analyzed by gas chromatography (Bentone and Unibed columns were used).

The rate of propane reaction at 773 K, over (Ga_2O_3 + H-ZSM-5) mixed powders was measured on samples having been submitted to the following treatments.

- Treatment A: calcination under O_2 at 773 K overnight.
- Treatment B: treatment A + calcination for 1 h under O_2 at 873 K.
- Treatment C: treatment B + reaction of propane for 5 min at 873 K.

Table 1
Propane conversion at 773 K. Catalyst weight 20 mg. Flow rate 2–5 ℓ/h. $P_{C_3H_8}$ = atmospheric pressure

Treatment	Rate of propane transformation (mmol h^{-1} g^{-1} catalyst)	Aromatic selectivity (% carbon basis)
A	88	0.5
B	93.3	0.5
C	264	18
D	257	15

– Treatment D: treatment B + reduction under hydrogen for 5 min at 873 K.

Table 1 summarizes the results. The rate of propane transformation was measured after 1 min on stream.

A significant difference in aromatization activity was detected on the originally oxygen-treated Ga_2O_3–H-ZSM-5 and on the sample which has been subjected to C_3H_8 at high temperature for 5 min. A threefold increase in reaction rate was observed for this latter sample. In addition, table 1 indicates that H_2-treated and C_3H_8-treated samples exhibit similar activity, although the H_2 partial pressures were different. From these results it is clear that the hydrogen produced during the first 5 min reaction of C_3H_8 is able to reduce Ga_2O_3 into suboxide gallium and to facilitate its migration into the zeolite channels. These results should be compared with those of Price et al. [2] showing that the migration of gallium species inside the zeolite channels under H_2 at 873 K is a rather fast phenomenon.

Thus, it appears that after 5 min on stream at 873 K, the solid is transformed by the H_2 product and it appears irrelevant to conclude that "there is no induction period during which the active sites are established" as stated in ref. [1].

Concerning the role of the addition of hydrogen to propane as described in ref. [1], it is difficult to derive any definitive conclusion since the experimental conditions are such that nearly 90% conversion is obtained for most of the catalytic runs; the inhibitory effect of H_2 on propane transformation was observed for Zn-H-ZSM-5 [3] and Ga-H-ZSM-5 [4] and has been explained by assuming that the limiting step of the propane dehydrogenation is the removal of hydrogen [5].

References

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