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

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The effects of co-feeding excess hydrogen on the propane aromatization reaction over Ga_2O_3, H-ZSM-5 and physical mixtures of Ga_2O_3 / H-ZSM-5 are described and discussed. For Ga_2O_3 alone co-feeding excess hydrogen gives a significant increase in the conversion and aromatic selectivity. For H-ZSM-5 alone co-feeding excess hydrogen gives a slight decrease in conversion and increases the selectivity to hydrogenated products. For Ga_2O_3/H-ZSM-5 physical mixtures co-feeding excess hydrogen leads to a significant decrease in the conversion and aromatic selectivity. We propose that hydrogen can be used as a reactive probe molecule for this reaction. Experiments are also described for propane aromatization over physical mixtures of powdered Ga_2O_3 and pelleted H-ZSM-5 that provide evidence for the reversible formation of the active site for this reaction.

Keywords: gallium oxide; zeolite H-ZSM-5; propane aromatization; synergy

1. Introduction

Catalytic reactions are considered to occur at *active sites* that have special properties due to the particular environment created at that location. Definition of the nature of active sites for a particular system has seen considerable progress when the three-dimensional structure of the catalyst is well defined, e.g. for alkane activation by enzyme catalysts such as cytochrome P450 [1], or by homogeneous molecular catalysts [2]. However, for many heterogeneous catalysts the surface structure is poorly defined and so the definition of the active site is also poor. This is particularly well exemplified by oxide catalysts for oxidation and dehydrogenation reactions where our understanding of active catalysts results from the observation of synergistic combinations of simple oxides that create catalysts with an activity far higher than that demonstrated by either of the simple oxides alone. Sometimes these synergistic combinations involve bulk compound formation, e.g. $(VO)_2P_2O_7$ for butane oxidation [3], but this is not typical and even then the *surface* structure of these compounds remains poorly defined [4]. For these catalysts it has been difficult to obtain information concerning the structure of the active sites and as a consequence the reaction mechanism is not well understood. For zeolites, however, the structure of the active site for acid catalysed reactions is well defined and can be readily studied by a number of in situ techniques. Hence these materials are well suited to realistic mechanistic studies. The propane aromatization reaction, in which propane is converted to benzene, toluene and xylenes, has received considerable research attention, since it represents a viable route for the activation of an alkane [5,6]. The preferred catalyst for this reaction is the zeolite H-ZSM-5 and the catalytic effect is significantly enhanced by the addition of gallium oxide. This promotional effect of gallium oxide can be observed either by ion exchange of the zeolite with aqueous gallium nitrate or simply by mixing the zeolite and oxide as powders [6,7]. The similarity of the catalytic effect obtained from these two very different preparation procedures is due to the observation that the hydrated gallium cation is too large to enter the microporous structure of the zeolite, and consequently both systems are considered to comprise gallium oxide and H-ZSM-5 as separate crystallites. We therefore consider this system to be ideal for the investigation of the nature of the active catalyst site, since it provides a very clear example of contact synergy [8,9] which results from a combination of mixing two separate compounds to obtain a catalyst with improved performance.

The reaction mechanism of propane activation has been the subject of many studies [6] and it is generally accepted that the reaction sequence involves the initial dehydrogenation of propane to propene which is subsequently oligomerized and aromatized. In addition there is a competing pathway involving acid catalysed propane cracking to give methane and ethane. The initial activation of propane is slow relative to the subsequent reactions and this can complicate the experimental investigation of the reaction mechanism. Recent studies by Iglesia [10,12] have shown that desorption of hydrogen, a major reaction product, plays a significant role in the overall kinetics of this process. Against this background we have investigated the effects of cofeeding excess hydrogen during the propane aromatization reaction and we have used this approach to investigate the nature of the active site for this reaction.

2. Experimental

Zeolite H-ZSM-5 was prepared by the method of Howden [13] with SiO_2/Al_2O_3 ratio of 35. Gallium was added by physically mixing β-Ga_2O_3 (Aldrich 99.99 + %) with H-ZSM-5 in various ratios.

Catalytic reactions were carried out using a stainless steel microreactor. Catalysts were initially heated to reaction temperature in flowing nitrogen. Following this the nitrogen flow was stopped and the catalyst was then exposed to the reaction gases that had been pre-stabilised via the reactor by-pass system. Analysis of the reactor effluent showed that no nitrogen was observed for samples taken at 5 min and so initial product distributions could be obtained at this reaction time. Product analysis was carried out by on-line gas chromatography. Reactant gases were either undiluted propane or propane diluted with nitrogen or hydrogen.

3. Results

Propane was reacted using either N_2 or H_2 as co-feed (propane : cofeed = 1 : 4) at 600°C over Ga_2O_3, H-ZSM-5 and Ga_2O_3/H-ZSM-5 physical mixtures formed by grinding the powders together. The results for the initial catalytic performance are given in table 1 and the addition of excess H_2 is observed to have the following effects. For the zeolite H-ZSM-5 alone, excess H_2 leads to a minor decrease in conversion but the decrease (3.2%) is close to the experimental error limits for these data (conversion data are accurate to 1%). There are also minor effects on selectivity and the selectivity to propene and aromatic products is decreased while the selectivities to methane and ethane are increased. For Ga_2O_3 alone co-feeding excess H_2 gives a significant increase in conversion and also causes the formation of aromatic products which are not observed in the absence of co-fed hydrogen. Although the total C_2 selectivity remains unchanged the ethane/ethene ratio is enhanced, a feature that is common for all the catalysts tested. In addition the selectivity to propane is decreased. For the catalyst containing 10% Ga_2O_3, H_2 cofeeding results in a significant decrease in conversion. For this catalyst H_2 cofeeding also results in a significant decrease in the selectivity to aromatic products and an increase in methane, ethane and propene. We therefore propose that hydrogen can be used as a reactive *probe* molecule, since specific effects are observed when the synergistic combination of gallium oxide and H-ZSM-5 is present (or absent) in this catalytic system.

A further series of experiments was done using a Ga_2O_3/H-ZSM-5 catalyst prepared by mixing 10% Ga_2O_3 as powder and 90% H-ZSM-5 as pellets (0.5 mm).

Table 1
Effect of excess hydrogen on propane aromatization [a]

Catalyst	Co-feed	Conv.	Product selectivity (mol%)				
		(%)	CH_4	C_2H_4	C_2H_6	C_3H_6	aromatics
Ga_2O_3	N_2	8.8	13.3	9.2	1.0	74.2	0
	H_2	21.8	13.2	2.3	10.6	71.9	0.7
H-ZSM-5	N_2	84.5	51.0	22.4	8.1	8.1	8.9
	H_2	81.3	54.2	21.3	10.6	7.0	5.8
10% Ga_2O_3/H-ZSM-5	N_2	95.4	46.6	9.8	10.5	2.7	30.4
	H_2	87.1	53.8	9.5	21.6	3.2	11.6

[a] Catalyst 0.5 g, 600°C, propane 10 ml min^{-1}, co-feed 40 ml min^{-1}, data are for initial time on line.

The mixture was formed by mixing the two reagents with gentle agitation in a glass tube. In these experiments the Ga_2O_3 (powder)/H-ZSM-5 (pellet) mixture was separately reacted with propane in the presence of either hydrogen or nitrogen as co-fed gases, using a standard laboratory microreactor. The experiments were conducted using nitrogen as an inert diluent to ensure that the experimental data for the absence of hydrogen could be collected for the same propane feedrate and reactant linear velocity through the catalyst bed. From the experimental data (fig. 1) it is evident that the effects expected for co-fed hydrogen are observed with respect to propane conversion. A sustained decrease in propane conversion is observed which is much more marked when the zeolite is used in pellet form than for the powder form (table 1). In addition, the expected effects on product selectivity, as listed previously, are also observed, i.e. for the Ga_2O_3/H-ZSM-5 mixture in the presence of hydrogen the selectivity to benzene, toluene and xylene was substantially decreased and selectivity for methane and ethane was increased. After 185 min reaction time the experiment was stopped and the catalyst was carefully removed from the reactor and sieved to remove the Ga_2O_3 powder as fully as possible. Subsequent analysis indicated that the H-ZSM-5 pellets that were obtained from the catalyst reacted with co-fed N_2 contained trace levels of gallium, so total removal was not possible under these conditions. The H-ZSM-5 pellets that were recovered by sieving were then reloaded to the microreactor and, in separate experiments, reacted for a further period with propane, together with either H_2 or N_2 as co-feed. The results (fig. 1) for the H-ZSM-5 that had been initially reacted with N_2 as the

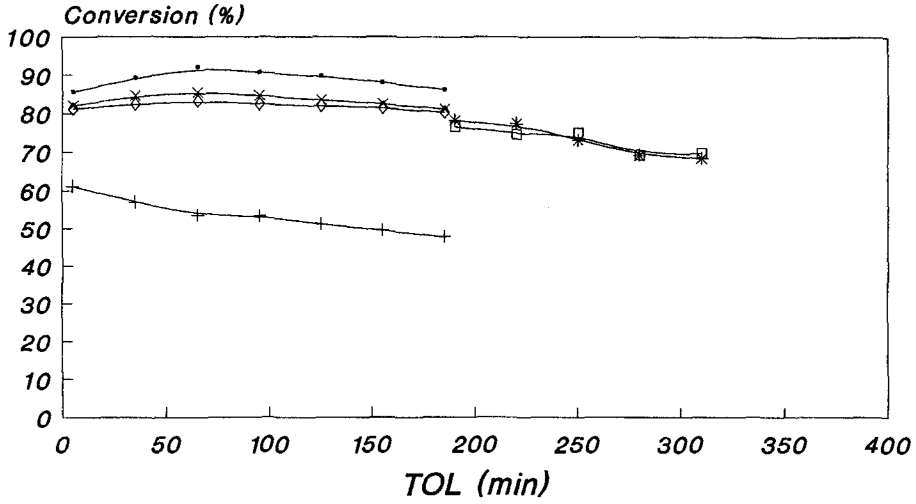

Fig. 1. Propane conversion versus time on line: 600°C, catalyst = 0.9 g H-ZSM-5 pellets and 0.1 g Ga_2O_3 powder; total flow rate = 50 ml/min; propane 20% by vol., balance N_2 or H_2. (■) Ga_2O_3/H-ZSM-5, N_2 co-feed; (+) Ga_2O_3/H-ZSM-5, H_2 co-feed; (*) H-ZSM-5 after removal of Ga_2O_3, N_2 co-feed; (□) H-ZSM-5 after removal of Ga_2O_3, H_2 co-feed; (×) H-ZSM-5 (no Ga_2O_3), N_2 co-feed; (◇) H-ZSM-5 (no Ga_2O_3), H_2 co-feed.

co-feed showed no effects on conversion when H_2 was used as the co-feed in the second stage and the conversions for the N_2 and H_2 co-feeds were identical within experimental error. The slight decrease in conversion observed after sieving is considered to be due to loss of catalyst mass since not all the zeolitic component could be successfully recovered by the sieving procedure. However, the selectivity to aromatic products (table 2), although decreased from the level observed for the mixed catalyst, was higher than that expected for H-ZSM-5 under these conditions. This effect may be due to the presence of the gallium that could not be removed by the simple sieving procedure adopted in this study.

4. Discussion

It is clear from these experiments that co-feeding excess hydrogen during propane aromatization has markedly different effects for H-ZSM-5, Ga_2O_3 and Ga_2O_3/H-ZSM-5. For H-ZSM-5 the addition of H_2 leads to a very small decrease in conversion and for Ga_2O_3/H-ZSM-5 a much more significant decrease. The effect is mainly due to the decrease in the formation of aromatic products and the formation of propene is not significantly affected. Recently, Iglesia et al. [10], using isotopic labelling, have shown that the initial activation of propane to propene is in equilibrium and that hydrogen atom recombination was the rate limiting process. In addition, it has been shown that hydrogen can be activated on the Brønsted acid sites of H-ZSM-5 [14]. Hence the observed effects in this study are consistent with these previous findings since the reaction of propane over H-ZSM-5 and Ga_2O_3/H-ZSM-5 gives H_2 as a major product and additional H_2 would not significantly influence the virtual surface pressure as described by Iglesia et al. [10]. As expected the main effect on selectivity with H-ZSM-5 and Ga_2O_3/H-ZSM-5 is a decrease in the formation of dehydrogenated products. For Ga_2O_3 the propane conversion is significantly enhanced which indicates that for this catalyst the

Table 2
Propane aromatization over Ga_2O_3(powder)/H-ZSM-5(pellet) [a]

Stage 1 co-feed	Stage 2 [b] co-feed	Time on line (min)	Selectivity [c] (mol%)				
			CH_4	C_2H_4	C_2H_6	C_3H_6	aromatics
N_2	none	5	47.2	17.7	8.7	5.7	19.9
	none	185	30.1	14.1	6.2	5.6	41.8
N_2	N_2	5	33.8	17.1	6.3	7.9	33.5
	H_2	5	46.3	16.3	12.2	6.6	17.6

[a] Reaction conditions: 600°C, propane 10 ml min^{-1}, cofeed 40 ml min^{-1}.
[b] After sieving to remove powder from the catalyst bed.
[c] Selectivity normalised excluding H_2.

hydrogenation of either a reaction intermediate or a carbonaceous coke precursor may be the rate limiting step.

A significant result of this study is that the catalytic data for the initial time on line indicate that the addition of Ga_2O_3 to H-ZSM-5 immediately leads to the formation of an active catalyst with conversion and selectivity that are not solely the sum of the individual components. It is apparent that there is no induction period during which the active sites are established. A number of previous studies [15,16] have considered that the active site is formed by reduction of Ga_2O_3 to a suboxide by hydrogen. The suboxide is known to be highly volatile and is therefore considered to be transported into the zeolitic structure forming the active site. Such a model would predict that the initial catalyst activity would be low and would increase substantially on reaction with hydrogen. This is clearly not observed and the increase in activity that is observed with increased reaction time is not substantial. It is therefore apparent that new high activity sites are present in the catalysts formed by physically mixing the two components before any substantial modification of the catalyst has occurred. It is possible that more than one active site configuration is present in these catalysts, with one site present initially and a further site being formed as a result of hydrogen treatment. However, the results presented here indicate that these additional sites (if they are formed or are chemically differentiated from those present in the initial physical mixture) are of similar overall activity to the initial sites since there is only a small increase in activity with reaction time. The activity and performance of these catalysts is dependent on the dispersion of the gallium oxide and this may be significantly improved either by continued reaction or by pretreatment with hydrogen for catalysts containing low concentrations of gallium, and this may account for the small improvement in catalytic performance with increased reaction time. In addition the experiments with the physical mixture of the powdered Ga_2O_3 and pelleted zeolite indicate that these sites can be formed, at least in part, reversibly. Hence it is considered that the active site in the Ga_2O_3/H-ZSM-5 physical mixtures can be represented by Ga^{3+} cations in gallium oxide in close proximity with the Brønsted acid site of the zeolite. At this site it is possible that the activation of propane occurs via one of two routes:

(a) propane is activated at the interface between the Ga_2O_3 and the zeolite,

(b) propane is initially activated on the gallium oxide and then an intermediate is transferred via the gas phase and subsequently reacted on the zeolite.

It is interesting to consider the hydrogen co-feeding results against the background of these two possibilities. It is clear that the effect of hydrogen on the Ga_2O_3/H-ZSM-5 physical mixtures is influenced by the size of the zeolite particles. When the larger pellets of H-ZSM-5 are used a much larger effect on conversion is observed compared to the results of the powder form of the zeolite. The system with the small particle size has a high degree of mixing with a relatively high concentration of active sites and in this case hydrogen addition has only a small effect. The system with the zeolite pellets is relatively poorly mixed and has a lower concentration of active sites. In the case of model (a) the effect of hydrogen could be expected to be inversely correlated with the active site concentration and in the case of (b) the effect of hydrogen would be correlated with the mean free path of a susceptible intermediate. Unfortunately on this basis both of the possibilities (a) and (b) are consistent with the experimental observations and hence the results of the present study are not informative in this respect. Earlier studies [17] based on the effect of Ga on product distributions indicated evidence consistent with model (a), but it is clear that further studies are needed. However, the present study does show that the active sites are present immediately on mixing Ga_2O_3 and H-ZSM-5 and furthermore that these sites can be formed reversibly.

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