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Aromatisation of propane over Ga/H-ZSM-5: comments on the activation of propane

Gavin J. Buckles, Graham J. Hutchings *

Leverhulme Centre for Innovative Catalysis, Department of Chemistry, University of Liverpool, PO Box 147, Liverpool, L69 3BX, UK

Abstract

The aromatisation of propane has been studied using Ga_2O_3, H-ZSM-5 and physical mixtures of Ga_2O_3/H-ZSM-5 as catalysts. Experiments using co-fed reactants of H_2, O_2 and NO are described, together with the use of 2-chloro-propane as a model reactant. The results are discussed in terms of a mechanism for the formation of the initial product propene in which propane is activated at the interface between the gallium oxide and the zeolite. The system is therefore an example of contact synergy and furthermore experiments are described that provide evidence for the reversible formation for the active site for this catalyst system.

Keywords: Aromatisation of propane; Ga/H-ZSM-5; Propane

1. Introduction

There has been continued interest in the design of catalysts for the effective utilisation of C_1–C_4 alkanes as chemical feedstocks. This interest is due to the wide availability of these alkanes either from natural gas and natural gas liquids, or as a refinery by-product. Since 1984 most effort has, without doubt, been devoted to the activation of methane, but as yet no success has been achieved that is of commercial significance [1,2]. In 1964 [3] it was noted that vanadium phosphate catalysts could activate butane under oxidising conditions to give high yields of maleic anhydride. Subsequently this has led to the commercialisation of this catalyst which is utilised in many production units around the world at the present time [4–6]. Both of the research approaches adopted for the activation of the C_1 and the C_4 hydrocarbons involved the use of dioxygen as a co-reactant since oxygenates were the desired products and also the formation of water as a by-product overcomes the severe thermodynamic limitations that exist for non-oxidative activation of C_1–C_4 alkanes [7]. However, it was known for some time that C_3–C_4 alkanes could be activated in the absence of dioxygen as co-reactant. If hydrocarbons, rather than oxygenates, are the desired product then the use of non-oxidising conditions could be preferred, since carbon loss as CO_2 cannot occur. Early work in this area by Csiscery [8] showed that alkanes could be dehydro-

* Corresponding author.

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cyclodimerised using bifunctional catalysts, e.g. Pt supported in acidic alumina. Coke formation with these catalysts resulted in their rapid deactivation and significant quantities of methane and ethane were produced as by-products. Zeolites were found to be active for alkane activation and Chen and Lucki [9] studied the disproportionation of alkanes using mordenite. Chen [10] and Cattanach [11,12] showed that the zeolite ZSM-5 could be used for the conversion of alkanes to aromatics. In particular, zinc-exchanged ZSM-5 was found to be effective in these early studies. Subsequently, research led to the development of gallium modified H-ZSM-5 as the most effective catalysts for C_3 and C_4 alkane aromatisation [13], and overall research in this field has led to the development of the Cyclar process [14,15].

In recent years there has been considerable academic interest in the mechanism of propane activation with zeolite catalysts and most workers consider that the activation involves a synergistic interaction between a gallium species and the zeolite. It is generally accepted that the reaction sequence involves the initial formation of propene via dehydrogenation. The propene is then oligomerised and aromatised; in addition, there is a competing pathway of acid catalysed propane cracking to give methane and ethane [14] which can be major by-products. A major problem concerning any mechanistic study of this system is that the initial dehydrogenation of propane to propene is slow relative to the secondary oligomerisation and aromatisation reactions. A similar situation is found in the conversion of methanol to hydrocarbons over zeolite catalysts when the rapid secondary reactions are a complicating factor in unravelling the reaction mechanism [16]. In our previous work on the mechanism of the methanol conversion reaction and the Fischer–Tropsch reaction, we used model reagents and reactive probe molecules to provide further mechanistic information [17–21]. We have developed this approach further in our studies concerning the activation of propane over Ga_2O_3/H-ZSM-5 and the purpose of this paper is to review the experimental work carried out in our laboratories and to comment on the mechanism of propane activation as well as the nature of the active site. In addition, recent studies using 2-chloro-propene as a model reactant as well as H/D exchange reactions will be described and discussed. Particular emphasis is placed on the initial reaction period and experimental conditions have been designed to explore the initial time on line.

2. Experimental

Zeolite H-ZSM-5 was prepared 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 gallium nitrate solution (0.05 M, 100°C for 24 h, zeolite dried at 100°C), or by physically mixing β Ga_2O_3 (Aldrich 99.99 + %) with H-ZSM-5 in various ratios.

Catalytic reaction 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, undiluted 2-chloro-propane or propane diluted with nitrogen, hydrogen, nitric oxide/nitrogen or oxygen/nitrogen.

2.1. Reaction of propane over Ga_2O_3, H-ZSM-5, Ga_2O_3/H-ZSM-5 and Ga-exchanged H-ZSM-5

H-ZSM-5 and gallium modified H-ZSM-5 catalysts were investigated for the propane aromatisation reaction and the results are given in Table 1. It is apparent that as the SiO_2/Al_2O_3

Table 1
Reaction of propane over Ga_2O_3, H-ZSM-5 and Ga_2O_3/H-ZSM-5

Sample [a]	Ga (%)	Conversion (% [b])	10^{-2} Product yield (mol h^{-1})	
			CH_4	BTX
Ga_2O_3	74.4	13.5	0.12	0.004
H-ZSM-5 (35)	0	79.2	2.7	1.1
Ga_2O_3/H-ZSM-5 (35)	3.7	83.6	2.2	1.3
Ga-ZSM-5 (35)	3.4	86.1	1.8	1.5
H-ZSM-5 (185)	0	19.6	0.71	0.007
Ga-ZSM-5 (185)	2.6	41.5	0.64	0.60
H-ZSM-5 (280)	0	6.7	0.21	0
Ga_2O_3/H-ZSM-5 (280)	3.7	9.0	0.12	0.01
Ga-ZSM-5 (280)	2.1	13.8	0.18	0.05

[a] Number in brackets indicates SiO_2/Al_2O_3 ratio; Ga_2O_3/H-ZSM-5 denotes physical mixture, Ga-ZSM-5 denotes ion exchanged sample.
[b] Reaction conditions: 600°C; propane, WHSV = 4.7 h^{-1}; 0.5 g catalyst.

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 aromatisation of reaction intermediates [14]. 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, and it is clear that the two methods lead to similar effects. 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 ($SiO_2/Al_2O_3 = 35$) gives a 3.5% 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 [21,22].

These experiments demonstrate that the effects of gallium promotion can readily be studied using simple physical mixtures and that this method enables different gallium levels to be studied. In a further set of experiments the use of a separate bed of Ga_2O_3 either upstream or downstream of a bed of H-ZSM-5 indicated that no improvement was observed in the catalytic performance of the H-ZSM-5. These results shown in Table 2 for the initial catalyst performance indicate that the Ga_2O_3 and H-ZSM-5 must be in close contact for the synergistic effect to be observed.

Table 2
Propane aromatisation over separate beds of Ga_2O_3 and H-ZSM-5 at 550°C and propane WHSV = 9.4 h^{-1}

Top bed	Bottom bed	Conversion (%)	Selectivity (mol%)					
			H_2	CH_4	C_2H_4	C_2H_6	C_3H_6	Aromatics
	H-ZSM-5	35.2	10.8	40.1	13.3	16.3	9.0	4.3
Ga_2O_3	H-ZSM-5	34.1	15.4	36.5	13.4	15.1	9.0	4.4
H-ZSM-5	Ga_2O_3	35.0	12.9	39.6	12.7	15.8	9.1	4.5

2.2. Effect of reactive probe molecules on catalytic performance

2.2.1. Effect of no co-feeding on propane conversion with H-ZSM-5 and Ga_2O_3/H-ZSM-5

The effect of continuous NO co-feeding on the aromatisation of propane in the presence of N_2 diluent over H-ZSM-5 at 550°C is shown in Fig. 1. In the absence of NO no decrease in propane conversion was observed with time on line. The presence of NO, however, led to a significant loss of conversion together with sustained deactivation. In addition, the selectivity to propene was enhanced by added NO, whereas the selectivities to aromatic and cracked products were decreased.

The effect of continuous NO co-feeding on the aromatisation of propane over Ga_2O_3/H-ZSM-5 physical mixture (5 mass% Ga_2O_3) was found to have a similar effect to that observed for H-ZSM-5 alone. In particular, the presence of NO leads to an enhancement in the selectivity to propene and a decreased selectivity for aromatics [23]. When the NO is removed from the feed gases the selectivities gradually approach those observed for the NO free reaction at similar time-on-line.

The effect of introducing short pulses of NO into the reactant gases was also studied and found to be informative (Fig. 2). The NO concentration during these short pulses was 5 mol%. It is clear that, as previously noted in the continuous NO feeding experiments, NO decreases propane conversion and that following each pulse the conversion does increase but it does not attain the level of the NO^- free reaction. The effect on conversion is related to the duration of the pulse time with longer times causing increased loss of conversion [23]. The effect on selectivity for these pulse experiments is shown in Fig. 3 and again it is clear that addition of NO leads to a reversible increase in the selectivity to propene and a reversible decrease in the selectivity to aromatic products. However, the time taken to recover the reaction selectivity following the removal of NO from the reacting gases was also found to be a function of the duration of the NO pulse and the longer the NO pulse, the longer the time required for recovery to be observed.

2.3. Effect of O_2 on propane aromatisation over H-ZSM-5

The effect of O_2 co-feeding (propane:N_2:O_2 = 10:9:1) on propane aromatisation at 550°C is shown in Fig. 4. In this experiment the O_2 was co-fed following the initial 95 min reaction of propane with N_2 as diluent (propane:N_2 = 1:1). During this initial reaction period there was a slight loss of conversion and yields of methane, propene and aromatic products. The introduction of O_2 leads to an increase in propane conversion but the deactivation rate was significantly enhanced. In addition the yield of propene was significantly increased, whereas the yields of methane, hydrogen and aromatic products were decreased. On removal of the O_2 from the reaction gases after 275 min. leads to an initial decrease in propane conversion after which the conversion recovers slightly. Removal of the O_2 leads to a decrease in the yield of propene whereas the yields of hydrogen, methane and aromatic products slowly increase.

2.4. Effect of H_2 on propane aromatisation over Ga_2O_3, H-ZSM-5 and Ga_2O_3/H-ZSM-5

Hydrogen pretreatment of propane aromatisation catalysts has been extensively studied [24–29] and more recently Iglesia and co-workers [30–32] has shown that hydrogen desorption plays a significant role in the overall kinetics of this process since hydrogen is one of the major reaction products. The effects of co-feeding excess hydrogen during the propane aromatisation reaction was investigated. Propane was reacted using either N_2 or H_2 as co-feed (propane:co-feed = 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 3 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

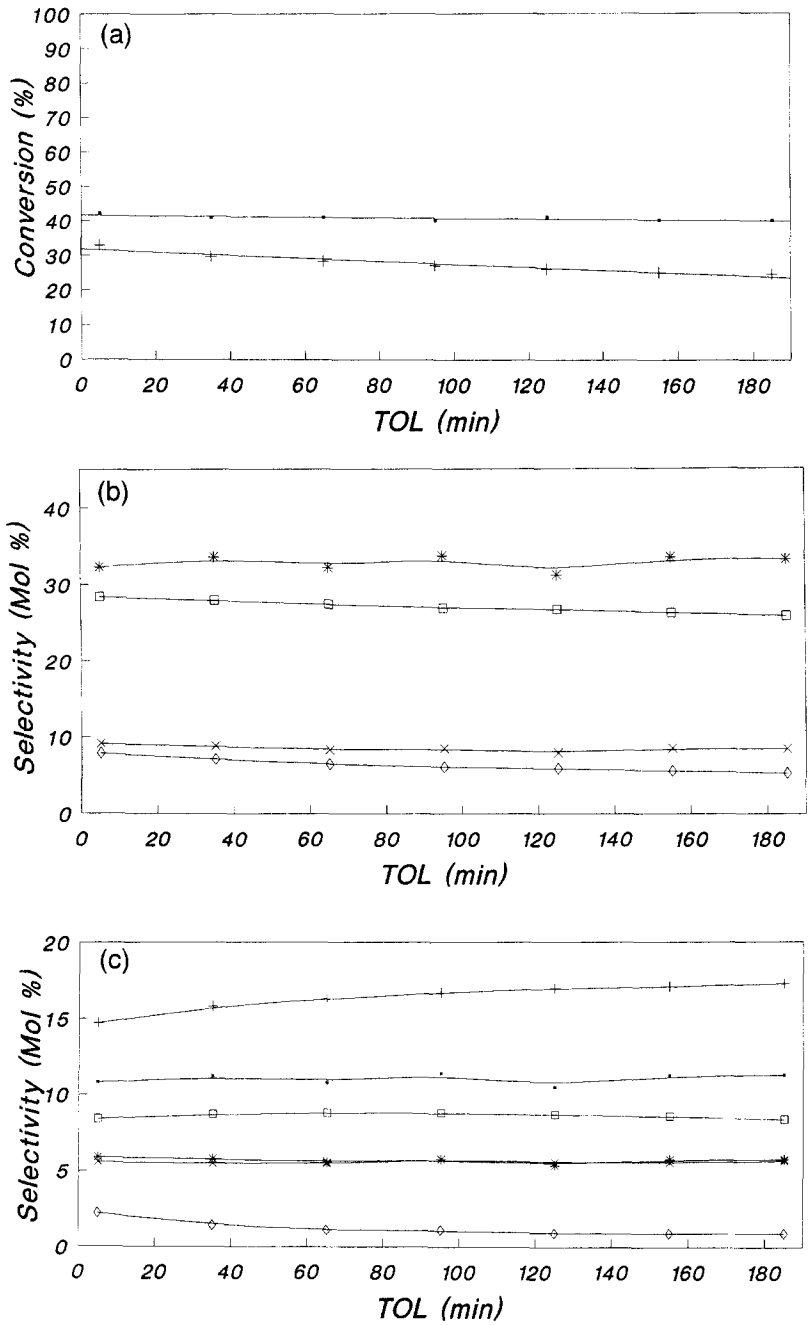

Fig. 1. Effect of NO co-feeding on propane aromatisation over H-ZSM-5 at 550°C. (A) ■, Propane conversion (propane:N_2 = 1:1); +, propane conversion (propane:N_2:NO = 10:9:1). (B) Effect on methane and ethane selectivity: *, CH_4; □, CH_4(NO); ×, C_2H_6; ◇, C_2H_6(NO). (C) Effect on alkene and aromatics selectivity: ■, C_2H_4; +, C_2H_4(NO); *, C_3H_6; □, C_3H_6(NO); ×, aromatics; ◇, aromatics(NO).

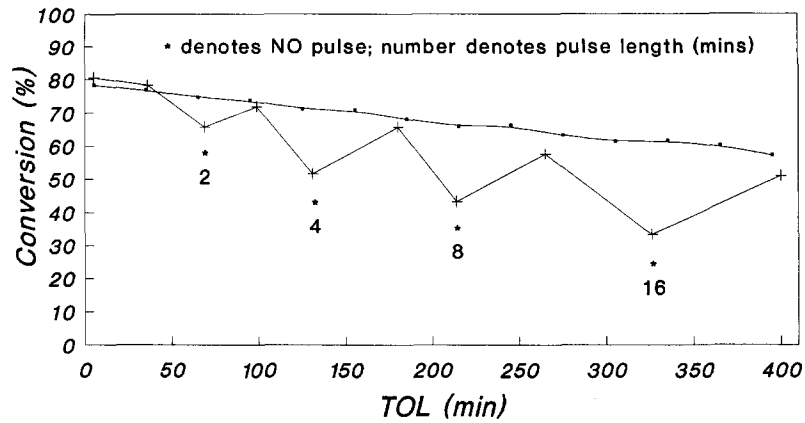

Fig. 2. Effect of NO pulses on propane conversion over Ga_2O_3/H-ZSM-5 at 600°C: ■, without NO; +, with NO.

(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 selectivity to methane and ethane are increased. For Ga_2O_3 alone co-feeding excess H_2 gives a significant increase in conversion and also facilitates the formation of aromatic products which are not observed in the absence of co-fed H_2. 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 propene selectivity is decreased. For the catalysts containing 10, 30 and 90% Ga_2O_3, H_2 co-feeding results in a decrease in conversion and the magnitude of this effect becomes more pronounced as the Ga_2O_3 content of the catalyst increases. For these catalysts H_2 co-feeding also results in a significant decrease in the selectivity to aromatic products and an increase in methane, ethane and propene. The addition of 1% H-

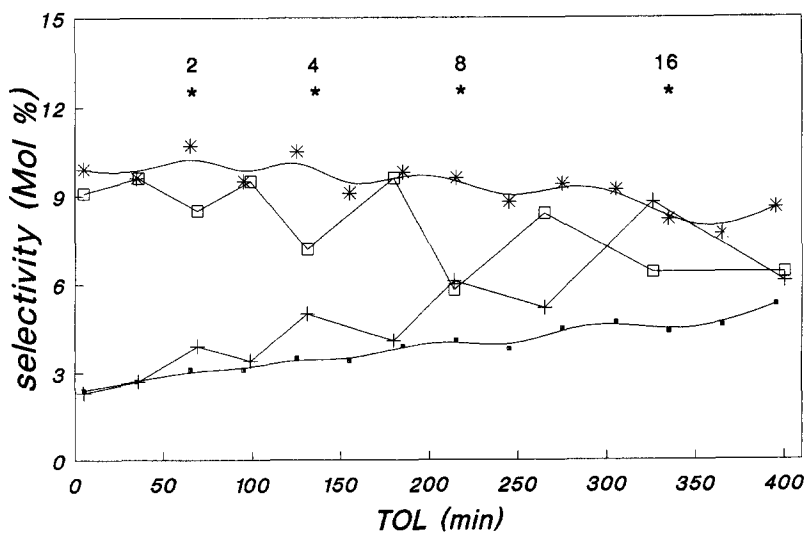

Fig. 3. Effect of NO pulses on propene and aromatic selectivity at 600°C: ■, C_3H_6; +, C_3H_6(NO); *, aromatics; □, aromatics(NO).

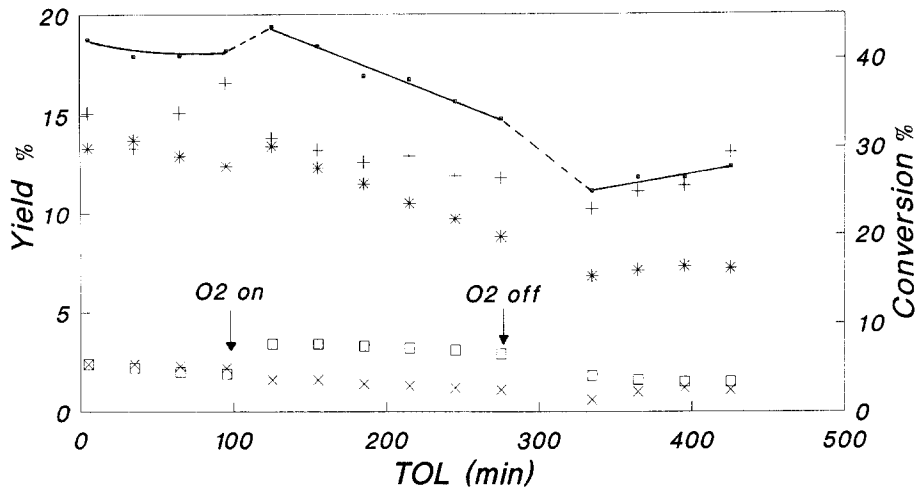

Fig. 4. Effect of O_2 co-feeding on propane aromatisation over H-ZSM-5 at 550°C, O_2 co-feeding started at 95 min and stopped at 275 min time on line. ■, Conversion; +, H_2; *, CH_4; □, C_3H_6; ×, aromatics.

Table 3
Propane aromatisation over Ga_2O_3, H-ZSM-5 physical mixtures [a]

Ga_2O_3 (%)	Co-feed	Conversion(%)	Selectivity (mol%) [b]				
			CH_4	C_2H_4	C_2H_6	C_3H_6	Aromatics
0	N_2	84.5	51.0	22.0	8.1	8.1	8.9
0	H_2	81.3	54.2	21.3	10.6	7.0	5.8
10	N_2	95.4	46.6	9.8	10.5	2.7	30.4
10	H_2	87.1	53.8	9.5	21.6	3.2	11.6
30	N_2	95.6	34.5	7.8	10.2	2.8	44.6
30	H_2	80.7	40.0	10.1	25.4	5.4	18.7
90	N_2	60.8	19.4	18.1	6.9	18.3	35.1
90	H_2	29.4	17.2	6.8	21.1	44.4	7.7
99	N_2	18.2	14.2	15.6	1.6	60.7	6.2
99	H_2	23.3	11.4	3.1	11.4	70.3	1.7
100	N_2	8.8	13.5	9.2	1.0	74.2	0
100	H_2	21.8	13.2	2.3	10.6	71.9	0.7

[a] Reaction conditions: 600°C; propane, 10 ml min^{-1}; co-feed, 40 ml min^{-1}.
[b] Selectivity normalized excluding H_2.

Table 4
Propane aromatisation over Ga_2O_3 (powder) H-ZSM-5 (pellet) [a]

Stage 1 co-feed	Stage 2 co-feed [b]	Time on line (min)	Selectivity (mol%) [c]				
			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
N_2	None	185	30.1	14.1	6.2	5.6	41.8
H_2	None	5	45.1	23.6	13.9	8.9	7.7
H_2	None	185	40.6	25.3	11.1	12.5	9.0
N_2	N_2	5	33.8	17.1	6.3	7.9	33.5
N_2	H_2	5	46.3	16.3	12.2	6.6	17.6
H_2	N_2	5	31.9	12.4	6.2	6.1	42.8
H_2	H_2	5	46.0	13.5	13.6	6.5	19.8

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

ZSM-5 to Ga_2O_3 results in a dramatic increase in conversion which is further enhanced by the presence of excess H_2. A similar set of experiments was subsequently carried using the same catalysts that had been pre-treated in H_2 at 550°C for 30 min. The results for the initial

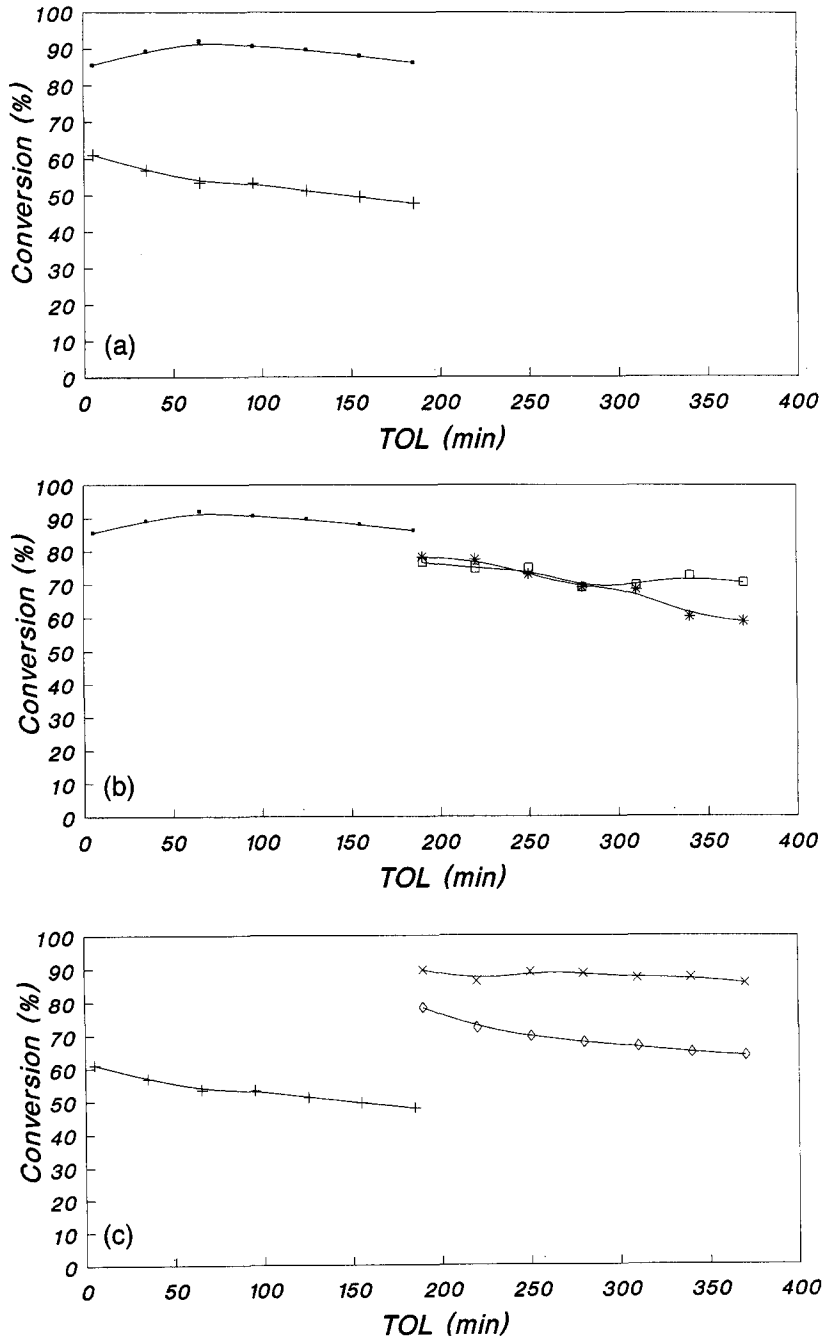

Fig. 5. Effect of H_2 co-feeding on propane aromatisation over Ga_2O_3(powder)/H-ZSM-5 (pellets) at 600°C. (A) Stage 1, reaction over Ga_2O_3/H-ZSM-5: ■, N_2; +, H_2. (B) Stage 2, reaction over H-ZSM-5 after sieving following reaction with N_2 diluent in stage 1: ∗, N_2; □, H_2. (C) Stage 2, reaction over H-ZSM-5 after sieving following reaction with H_2 diluent in stage 1: ×, N_2; ◇, H_2.

reaction period demonstrated similar effects to those observed for the non-pre-treated materials when excess H_2 is co-fed [23].

2.5. Evidence for the reversible formation of a catalytic active site for the synergistic combination of Ga_2O_3 / H-ZSM-5

Experiments were conducted with a catalyst prepared by the mixing of 10% Ga_2O_3 powder with 90% H-ZSM-5 pellets (0.5 mm pellet size). These two materials were mixed using gentle agitation in a glass tube and no grinding was used, as had been the procedure concerning the preparation of the physical mixtures used in the previously described studies. In a series of experiments this catalyst was reacted separately with propane in the presence of co-fed N_2 or H_2 (propane:co-feed = 1:4; total flow rate = 50 ml min^{-1}). The results are detailed in Table 4 and Fig. 5. It is clear that the effects previously noted for H_2 co-feeding are apparent. After 185 min time-on-line, the experiment was stopped and the catalyst was removed with great care from the reactor. The used catalyst was then sieved to remove as much as possible of the Ga_2O_3 powder from the H-ZSM-5 pellets. Analysis of the H-ZSM-5 used in the N_2-co-fed experiment showed trace levels of gallium were present so clearly it is not possible to remove all the Ga_2O_3 from the H-ZSM-5 using this simple procedure, however it was confirm that virtually all but trace amounts had been removed.

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. 5) for the H-ZSM-5 that had been initially reacted with N_2 as the co-feed showed no effects on conversion when H_2 was used as the co-feed in the second stage and the conversion 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 4), 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 method. The results for the H-ZSM-5 that had been initially reacted with H_2 as co-feed are also shown in Fig. 5. It is clear that following the removal of the Ga_2O_3 powder, by the sieving procedure, the conversion of propane is increased for both N_2 and H_2 as co-feeds. However, there is a significant decrease in the conversion for the H_2 co-feed when compared with the N_2 co-feed. Such behaviour is characteristic of Ga_2O_3/H-ZSM-5 mixtures (Table 3) and the selectivity data are also consistent with this observation. These experimental data therefore provide a simple demonstration that a high activity site can be created in a physical mixture of Ga_2O_3 powder and H-ZSM-5 pellets and that these sites can be largely removed by removing the Ga_2O_3 from contact with the H-ZSM-5. It should be noted that these catalyst systems were specifically designed to maintain the segregation of the Ga_2O_3 and the zeolite so that the synergy between these two components can be effectively demonstrated. In a working catalyst designed for maximum aromatics production it is necessary to maximise this contact synergy by dispersion of the Ga_2O_3 throughout the pore structure of the zeolite and this is aided by sustained hydrogen pretreatment or prolonged use in the reactor.

2.6. Reaction of 2-chloro-propane as a model reactant

In many mechanistic discussions it is considered that the initial C–H bond activation in propane is the most difficult step. To probe this aspect further we have investigated the replacement of a C–H bond with a C–Cl bond which is know to be more facile towards cleavage.

2-chloro-propane was separately reacted in the absence of a catalyst as well as in the presence of Ga_2O_3 and H-ZSM-5 separately and the results are shown in Table 5 for the initial time-on-line data. It is clear that with 2-chloro-propane there is an appreciable blank gas phase reaction that is not observed with propane under equivalent reaction conditions, confirming the enhanced reactivity of this substrate. In this gas phase reaction, the only carbon containing product is propene formed via an elimination reaction. There are, however, interesting differences concerning the reaction of 2-chloro-propane over Ga_2O_3 and H-ZSM-5. After making allowance for the gas phase reaction it is clear that the conversion of 2-chloro-propane is enhanced by both the presence of Ga_2O_3 and H-ZSM-5. The difference in reactivity displayed by these two materials is very small (difference in conversion between catalysed and gas phase reaction = 17% and 27% for Ga_2O_3 and H-ZSM-5, respectively). This is significantly different from the reaction of propane over Ga_2O_3 and H-ZSM-5 under similar reaction conditions when it is observed that H-ZSM-5 is more than an order of magnitude and more reactive. There are also significant differences concerning the selectivity of the products with the catalysed reaction. For Ga_2O_3 the products are mainly propene together with some C_6 and other coupling products. This is very similar to the reaction of propane over Ga_2O_3 when propene is the major product. For H-ZSM-5 there are interesting differences between the reaction of propane and 2-chloro-propane. For 2-chloro-propane it is found that the products are mainly propane (a H-rich product) together with some benzene (a H-poor product). This is in contrast to the reaction of propane over H-ZSM-5 when the major products are methane and ethane formed via an acid catalysed cracking reaction.

These data can be rationalised in the following way. Reaction of 2-chloro-propane over Ga_2O_3 and H-ZSM-5 leads initially to the formation of the $C_3H_7^+$ cation. This then dimerises to give C_6 products over Ga_2O_3, whereas over H-ZSM-5 the possibility of dimerisation and H-transfer reactions are both possible and the $C_3H_7^+$ cation abstracts H^- from the C_6 dimerisation product to form propane. The products over Ga_2O_3 are therefore the product of dehydrogenation, whereas the products over H-ZSM-5 are those of cyclisation and hydrogen transfer. These selectivity differences are very similar to those observed for the reaction of propane over Ga_2O_3 and H-ZSM-5 and indicate that 2-chloro-propane can be considered as a useful model reactant. The key result from these model reactant studies is that by replacing a C–H bond, that is known to be difficult to activate, with a C–Cl bond, that is more facile to active, similar reactivities are observed over Ga_2O_3 and H-ZSM-5, whereas propane displays considerably different reactivities over Ga_2O_3 and H-ZSM-5.

2.7. Model experiments using CH_4/D_2 exchange reactions

In a related study concerning the scientific design of catalysts for the oxidation of methane to methanol some interesting results have been

Table 5
Reaction of 2-chloro-propane over Ga_2O_3 and H-ZSM-5

Catalyst [a]	Conversion	Product selectivity (mass %)					
		C_1/C_2	C_3H_6	C_3H_8	C_4/C_5	C_6	Aromatics
None	67.3	0	99.6	0	0.3	0.1	0
Ga_2O_3	85.0	0.5	38.3	5.9	18.5	16.8	0
H-ZSM-5	95.0	5.2	4.4	50.6	34.4	1.9	3.5

[a] Reaction conditions: 425°C; 0.5 g catalyst; WHSV = 1.8 h^{-1}; nitrogen diluent, 20 ml min^{-1}.

observed [33]. The full experimental details are listed elsewhere [34]. It was decided to investigate the CH_4/D_2 exchange reaction over simple oxides as an indication of the ability of the oxide to activate hydrocarbons. These data were then used together with two other key catalyst design parameters [35], namely (a) the stability of methanol over the simple oxide under oxidising conditions and (b) the rate of the $^{18}O_2/^{16}O_2$ exchange reaction over the simple oxides.

At 500°C, a temperature at which the Cyclar reaction can be observed, it was found that the rate of CH_4/D_2 exchange reaction was highest over Ga_2O_3 (4.71×10^{19} molecules s^{-1}) and ZnO (5.57×10^{17} molecules s^{-1}), whereas virtually all other simple oxides gave an exchange rate of 10^{15}–10^{16} molecules s^{-1}. Even when these data are corrected for surface area effects the gallium oxide and zinc oxide are by far the most effective catalysts for the activation of methane via the CH_4/D_2 exchange reaction. The main product was found to be CH_3D indicating mono-exchange to be the dominant process. A key step in this exchange reaction is the initial polarisation of the C–H bond to give heterolytic bond fission. These data may provide an indication as to why Ga_2O_3 and ZnO are the preferred catalyst components for the activation of propane over modified H-ZSM-5 catalysts. In addition, these data provide further evidence that the key role of Ga_2O_3 and ZnO in these catalysts is to aid C–H bond activation via heterolytic cleavage caused by bond polarisation induced by the Ga_2O_3 and ZnO.

2.8. Comments on the nature of active site and the reaction mechanism of propane activation

It is considered that the data presented for the co-feeding of NO, O_2 and H_2 as co-reactants, together with the use of 2-chloro-propane as a model reactant can provide key insights into the nature of the reaction mechanism with this catalyst.

Co-feeding NO leads to a rapid loss of propane conversion, but as was demonstrated by the NO pulse experiments, the recovery in conversion observed on NO removal is not rapid and does not return to the level prior to NO addition. Similar effects are also apparent for the selectivity data. This indicates that NO is not acting as a radical scavenger in the propane aromatisation reaction, since if this were to be the case then the recovery in catalytic performance would also have been immediate as is observed for methane coupling [36] which is generally agreed to involve radical intermediates. Hence it can be concluded that the intermediates in the propane aromatisation reaction do not involve radical species. Since NO leads to a loss in activity which only slowly recovers when NO is removed, it is most probable that NO is acting as a catalyst poison as has been observed for the effect of NO on the methanol conversion reaction over H-ZSM-5 [17,18]. The poisoning effect is observed for the zeolite in the absence of gallium, although it is more pronounced for Ga_2O_3/H-ZSM-5 which may be related to the higher activity of this catalyst. Co-feeding NO also leads to a decrease in the yields of cracked products, e.g. methane and aromatic products. This indicates that NO interacts with the Brönsted acid sites known to be involved in the formation of these products. This interaction could be linked to the deactivation process since NO could react with propane or another hydrocarbon to form a nitrogen containing molecule that would act as a potent catalyst poison.

Co-feeding O_2 during the propane aromatisation reaction provides further evidence concerning the activation of propane. The introduction of O_2 in the presence of H-ZSM-5 leads to an immediate increase in the yield of propene and a decrease in the yield of H_2. These observations are consistent with propene formation from propane being equilibrium controlled with O_2 reacting with H_2 thereby enabling increased propane conversion. In addition the addition of O_2 causes significant deactivation to occur, possibly via coke formed by the polymerisation of hydrocarbon oxidation products. However, the

deactivation is partially reversed on removal of O_2 and the product yields recover towards the levels expected in the absence of O_2. Oxygen co-feeding also causes the yields of methane and aromatic products to decrease This effect is similar to the effects of NO and indicates that both these reagents interfere with the acid catalysed cracking, oligomerisation and aromatisation reactions, whereas NO does not affect the selective activation of propane to propene and O_2 enhances this reaction by removing H_2.

The effects of co-feeding H_2 are different 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. This is not unexpected since in 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 markedly increase the virtual surface pressure as described by Iglesia et al. [30]. The excess H_2 adversely influences the formation of dehydrogenated products and it has been recently shown that molecular hydrogen can be activated by the Brönsted acid sites of H-ZSM-5 and that the zeolite possesses hydrogenating activity [37].

If we consider the reaction of propane over H-ZSM-5 alone the products are mainly those of propane cracking together with some propene and aromatic hydrocarbons. In the absence of any additive oxides it is most probable that the active site is the Brönsted acid bridging hydroxyl groups. Propane activation can be considered to occur in either of three ways:

1. abstraction of $H\cdot$ to form $C_3H_7\cdot$
2. addition of H^+ to form $C_3H_9^+$
3. abstraction of H^- to form $C_3H_7^+$.

The abstraction of a hydrogen atom to form a radical intermediate (pathway 1) can be discounted since NO, which is a known radical scavenger, does not significantly affect the formation of propene. For H-ZSM-5 it is considered that the major pathway is via the addition of H^+ which would lead to the formation of either a primary or a secondary carbonium ion. The primary carbonium ion would react to form methane and $C_2H_5^+$, which would react subsequently to give ethane or ethene, more readily than loss of H_2 to form a primary $C_3H_7^+$ intermediate. The secondary carbonium ion would not be expected to form ethane and CH_3^+ but could lose H_2 to form a secondary $C_3H_7^+$ intermediate that would subsequently form propene, a necessary precursor for the formation of aromatic products. It therefore possible that activation of the propane by the Brönsted acid sites could lead to the formation of both the cracked as well as the selective products.

When the gallium oxide is added to the zeolite it is possible that these zeolite catalysed reactions still occur at unmodified Brönsted acid sites. However, the catalyst activity and aromatic yield is so markedly promoted that it is apparent that new active sites are now involved. We have shown that the initial activity of the Ga_2O_3/H-ZSM-5 physical mixtures is markedly different than those of the oxide and the zeolite separately. This represents an example of contact synergy which has been well documented previously for oxide catalysts [38,39]. It can therefore be considered that new high activity sites are present before any substantial modification of the catalyst has occurred. The activity and performance of these catalysts is dependent on the dispersion of the gallium oxide and this can be significantly improved either by continued reaction or by pretreatment with hydrogen for catalyst containing low concentrations of gallium. 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 Brönsted 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 gal-

lium 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 (compare data for 10% Ga_2O_3/H-ZSM-5 in Table 3 and Fig. 5A). 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 [40] 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, our results do 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.

Concerning the mechanism of activation we have proposed that the propane is activated at the interface between Ga_2O_3 and the zeolite Brönsted acid site (i.e. pathway (a)). The initial process is the polarisation of the C–H bond by Ga_2O_3. Evidence in support of this proposal is provided by the results of the CH_4/D_2 exchange reaction and the experiments using 2-chloro-propane as the model reactant. In addition, infra-red spectroscopy studies have indicated that C–H bond polarisation can occur over this oxide [41]. Subsequently, the polarised C–H bond is cleaved by interaction with the zeolite Brönsted acid site as shown in Fig. 6, in a reaction that is analogous to that considered to occur in propane cracking over zeolite catalysts [42]. Hence, the central role of Ga_2O_3 is to enable C–H bond polarisation to be induced so that the C–H bond becomes susceptible to reaction with the zeolite Brönsted acid site. In this way the gallium oxide and the zeolite are considered to act in concert at an active site that is located at the interface between the two phases.

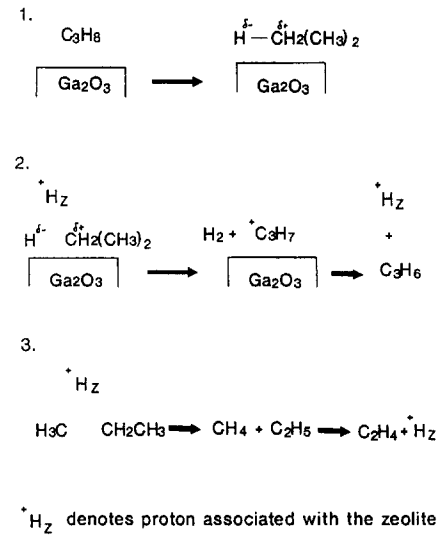

Fig. 6. Proposed mechanism of propane activation on Ga_2O_3 /H-ZSM-5.

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