PROPANE CONVERSION OVER ZEOLITE CATALYSTS: COMMENTS ON THE ROLE OF Ga

Gavin BUCKLES, Graham J. HUTCHINGS * and Craig D. WILLIAMS

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

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The activation of propane using zeolite H-Y and Ga^{3+} exchanged zeolite Y indicates that in the presence of Ga^{3+} the mechanism of propane activation is changed from a cracking pathway to a dehydrogenation pathway. The presence of both Ga^{3+} and H^+ are required to achieve this effect.

Keywords: Propane activation, zeolite Y, gallium oxide, propane cracking, propane dehydrogenation

1. Introduction

The conversion of light alkanes into aromatic compounds is of potential industrial interest for the production of petrochemicals and chemical intermediates. The process concept was first disclosed by Csiscery [1] in 1970 who described dehydrocyclodimerisation of alkanes to aromatics using bi-functional catalysts, eg. Pt supported on an acidic alumina. Chen [2] and Cattanach [3,4] showed that the pentasil zeolite ZSM-5 could also be used to convert aliphatic compounds into aromatics. Subsequent studies by Davies and Kolombos [5] showed that the alkane conversion could be improved if gallium was used as a promoter for ZSM-5. Since these early studies a considerable volume of research has been completed and this has recently been reviewed by Seddon [6]. A number of studies have attempted to determine the role played by the gallium promoter, but these have lead to conflicting conclusions. Kitagawa et al. [7,8] considered that the gallium does not directly participate in the activation of propane, but efficiently converts the intermediate alkenes into aromatic hydrocarbons. However, Gnep et al. [9] concluded that gallium did play a role in the direct activation of the alkane. One of the possible causes of these conflicting conclusions is that with the zeolite catalyst ZSM-5 the secondary conversion reactions of the intermediate alkenes are far more rapid than the initial alkane activation. For example, ZSM-5 can oligomerise propene, the proposed primary product from propane conversion, at temperatures in the region 200–250 °C, whereas activation of propane over ZSM-5 only becomes significant at much higher temperatures > 500 ° C. Hence, for the Ga/ZSM-5 system the rapid secondary chemistry masks the primary chemistry making it difficult to make definitive statements concerning the reaction mechanism. For this reason we have studied a zeolite which is less active for this reaction, an ultrastabilised zeolite Y, in an attempt to minimise the effect of the secondary chemistry. However, the major advantage, with respect to the selection of this zeolite, is that with zeolite Y it is well known that the acid sites can be tailored, ie. the relative proportion of Bronsted and Lewis acid sites, by choice of calcination temperature [10]. This is not readily possible with H-ZSM-5 and, hence, zeolite Y can be used to investigate the role of gallium and acidity in this conversion process.

2. Experimental

2.1. CATALYST PREPARATION

Ultrastable zeolite Y (LZY 82, Union Carbide) was calcined at 550 ° C or 700 ° C for 16 h prior to being pelleted, crushed and sieved to give particles (1.0 mm) suitable for testing in the catalytic reactor. Gallium doped zeolite Y catalysts, denoted Ga-Y, were prepared by ion exchange. Uncalcined zeolite Y (10 g) was suspended with stirring in 100 ml of an aqueous solution of gallium nitrate ($Ga(NO)_3.xH_2O$, Aldrich 99.9%, 0.05 M) at 100 ° C for 4 h. The zeolite was recovered by filtration, washed with distilled water, dried (110 ° C, 12 h). The procedure was repeated a further two times. The sample was then calcined at 550 ° C prior to being pelleted, crushed and sieved as for the undoped samples. Analysis of the sample indicated that 5.6% Ga was present in this sample by this procedure.

2.2. CATALYST TESTING

The reactions were carried out using a continuous flow stainless steel microreactor at atmospheric pressure. Catalysts were initially brought to reaction temperature in a flowing dry N_2 atmosphere and then propane was fed to the reactor at a controlled feedrate ($WHSV = 4.7\ h^{-1}$) in the absence of diluent and reacted over the zeolite catalysts (0.5 g) at 600 ° C. The reactor bed dimensions were diameter 10 mm, length 10 mm. The total reactor effluent gases were analysed with on-line gas chromatography using both flame ionisation and thermal conductivity detectors. Blank thermal reactions of propane in the absence of the zeolite catalyst were found to be negligible and Na exchanged zeolite Y tested under similar conditions demonstrated a steady conversion level of ca 5%. Satisfactory mass balances were obtained for all data presented.

3. Results and discussion

3.1. CONVERSION OF PROPANE OVER ZEOLITE Y

The conversion of propane was carried out at 600 ° C over zeolite Y calcined at 550 ° C and 700 ° C, and the results are shown in figs. 1 and 2. As expected, zeolite Y exhibits only a short lifetime for this reaction and the conversion of the sample pre-calcined at 550 ° C declines from 31% to 6% in the first hour, which is in distinct contrast to the much longer lifetime exhibited by ZSM-5 [6]. During this reaction period the product selectivity changed markedly and in particular the selectivity to methane and C_2 hydrocarbons falls with decreasing conversion, while the selectivity to propene increases slightly. At all times the selectivity to aromatic compounds (benzene, toluene and xylene) is very low $< 1\%$, but in line with the short lifetime, the overall selectivity to coke is ca 27%. The high selectivity to coke is a result of the lack of shape selectivity and higher density of acid sites for this zeolite when compared to H-ZSM-5.

Zeolite Y pre-calcined at 700 ° C demonstrates much lower initial activity, although the selectivity trends are similar to those of zeolite Y pre-calcined at 550 ° C. Calcination of zeolite Y at 700 ° C is well known to cause dehydroxylation of the Bronsted acid sites and consequently lead to the formation of Lewis acid sites [10]. Hence, the sample pre-calcined at 700 ° C will have a lower initial concentration of Bronsted acid sites, and since this sample demonstrates lower initial activity, it can be concluded that for the undoped zeolite Bronsted acid sites are necessary for propane activation. Since the major products are initially methane, ethane and ethene it is apparent that propane activation in the undoped zeolite occurs via protonation followed by cracking, as proposed for undoped H-ZSM-5 by Kitagawa et al. [7]. However, it is also interesting to note that the zeolite Y pre-calcined at 700 ° C and the deactivated Bronsted acid form exhibit

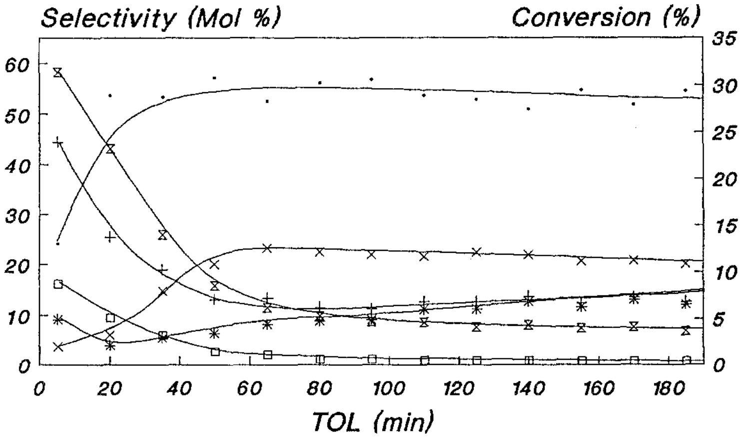

Fig. 1. Propane conversion over zeolite Y calcined at 550 ° C: ⧖ propane conversion; product selectivies: ■ H_2, + CH_4, * C_2H_4, □ C_2H_6, × C_3H_6.

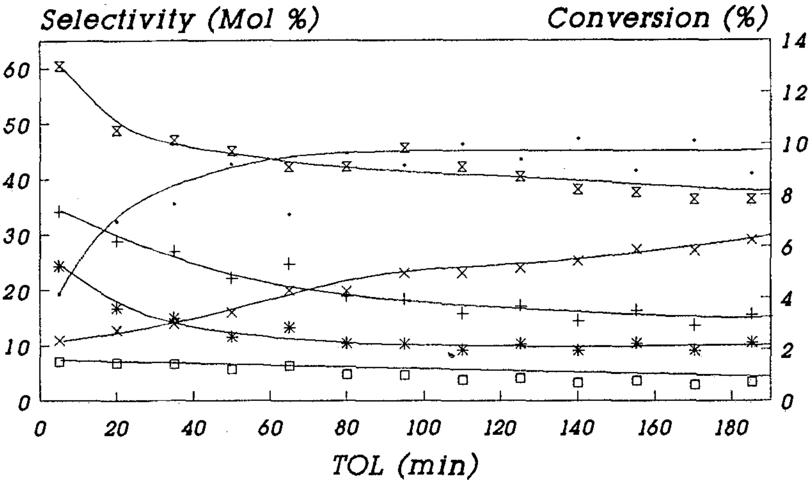

Fig. 2. Propane conversion over zeolite Y calcined at 700 ° C, key as fig. 1.

similar propane conversions and product selectivities. This activity is very similar to the performance of the Na exchanged form of this zeolite precalcined at 550 ° C. This may indicate that part of the reaction is gas phase in nature, ie. radical reactions initiated by collision of propane with the internal pore structure of the zeolite. However, as the ultrastabilised form of zeolite Y utilised in this study contains some non-framework aluminium, it is possible that this residual low level of propane activation is due to the presence of Lewis acid sites, rather than due to radical initiation. The present data cannot be used to distinguish between these two effects. However, it is interesting to note that strong Lewis-base pairs have recently been proposed [11] as active centres in modified pentasil zeolites capable of C–H bond polarisation and propane activation.

3.2. CONVERSION OF PROPANE OVER Ga-Y

The conversion of propane was carried out at 600 ° C over Ga^{3+} exchanged zeolite Y which had been pre-calcined at 550 ° C, and the results are shown in fig. 3. Initial inspection of these results indicates that the Ga exchanged zeolite appears to be slightly less active than the undoped zeolite which could imply that for this system Ga has no marked effect on propane activation. However, in a separate experiment, zeolite Y was treated with water in an analogous procedure at the same pH to that used in the Ga^{3+} exchange preparative method. Catalyst testing of this material (fig. 3) gave propane conversions very similar to those obtained for the Ga exchanged material. The loss in conversion observed is considered to be due to de-alumination, a process well-known for zeolite Y [12], rather than the exchange of H^+ by $Ga(H_2O)_6^{3+}$. However, de-alumination of zeolite Y in this way was not found to effect the product selectivity observed from propane activation. These results therefore indicate that addition of Ga to zeolite

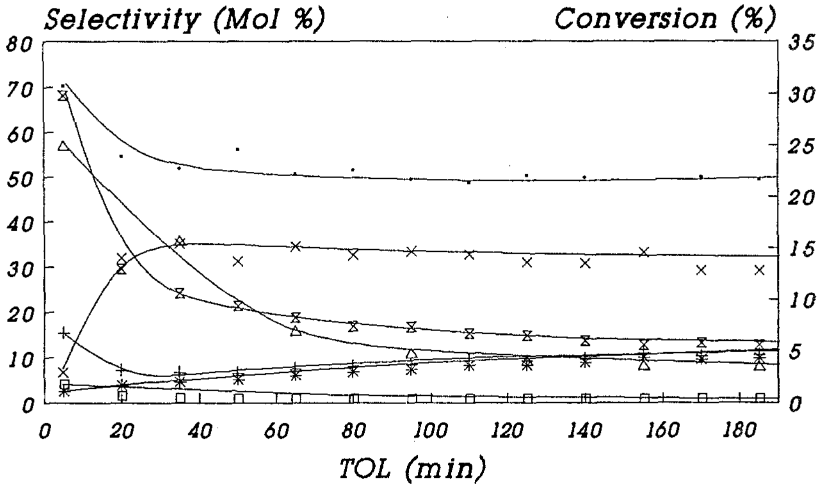

Fig. 3. Propane conversion over gallium exchanged zeolite Y calcined at 550 ° C: ⧖ propane conversion over gallium exchanged zeolite Y, △ propane conversion over zeolite Y treated at same pH as gallium exchange procedure; product selectivities: ■ H_2, + CH_4, * C_2H_4, □ C_2H_6, × C_3H_6.

Y does not markedly affect the overall level of propane activation. However, Ga does significantly affect selectivity (fig. 3) and the main effect of Ga addition is to decrease the formation of cracked products and increase the formation of hydrogen and propene. In the presence of Ga the selectivity to aromatic products or coke is not significantly enhanced and the overall selectivity to coke is decreased to 13%, compared to the undoped zeolite which indicates that the Ga does not promote the oligomerisation of the primary alkene product. In addition, the C/H ratio of the coke is increased in the presence of Ga (zeolite Y (pre-calcined at 550 ° C) coke C/H = 0.076; zeolite Ga-Y (pre-calcined at 550 ° C) coke C/H = 0.057) which is in agreement with the much higher selectivities to hydrogen observed with the Ga-Y catalysts.

For the zeolite ZSM-5 it is considered that the hydrated Ga^{3+} cation cannot enter the microporous structure due to the size constraints [11]. Although zeolite Y has a considerably larger window size, entry of the hydrated cation may still be impeded by the charge imbalances caused by compensation of isolated negative charges of the framework by the trivalent cation. Consequently it can be expected that the Ga^{3+} cations are most likely located on the exterior of the zeolite microcrystallites. In addition, it is also known for ZSM-5 that the method of addition of the gallium promoter is not particularly important and similar results can be achieved using ion exchange and impregnation methods [13]. To examine this aspect for the Ga-Y system, zeolite Y pre-calcined at 550 ° C and 700 ° C was separately mixed with Ga_2O_3 (5% by mass, Aldrich 99.9%). The results of propane conversion for the 5% Ga_2O_3 (550 ° C) catalyst (fig. 4) are very similar to those obtained for Ga-Y prepared by the cation exchange method (fig. 3). This

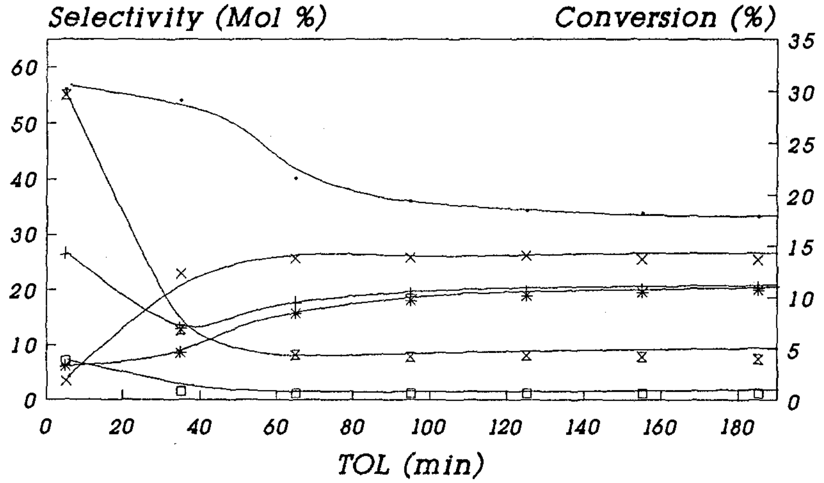

Fig. 4. Propane conversion over 5% Ga_2O_3/zeolite Y calcined at 550 ° C, key as fig. 1.

confirms that the method of Ga addition to zeolite Y is also not important in achieving the overall catalytic effect. In a separate experiment the conversion of propane over Ga_2O_3 in the absence of zeolite Y gave mainly propene and hdyrogen as products, but at a much lower activity when compared to the Ga_2O_3/zeolite Y system. To ascertain whether it was the combination of the Ga_2O_3 with the zeolite structure or the combination of Ga_2O_3 and the Bronsted acidity of the zeolite, the results of the experiment with the 5% Ga_2O_3/Y (700 ° C) catalyst (fig. 5) are most significant. Addition of Ga_2O_3 to the zeolite with the decreased Bronsted acidity is not found to enhance the catalyst performance. It can therefore be concluded that for effective propane activation to propene and hydrogen as primary products the combination of Ga^{3+} and

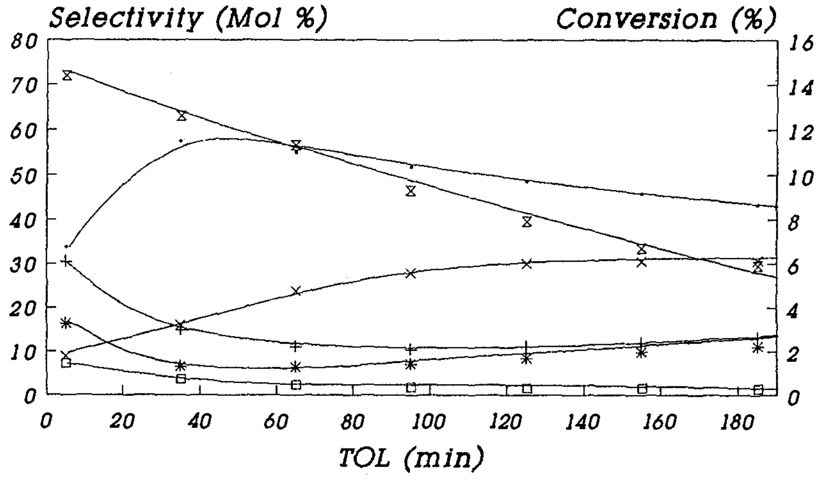

Fig. 5. Propane conversion over 5% Ga_2O_3/zeolite Y calcined at 700 ° C, key as fig. 1.

Table 1
Initial product yields

Catalyst	Time on line (min)	Propane conversion %	Product yields (g/min)							BTX [a]
			H_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_4	C_5	
H-y [b]	5	31.3	2.6×10^{-4}	3.9×10^{-3}	1.4×10^{-3}	2.6×10^{-3}	8.4×10^{-4}	$6\ \times10^{-4}$	4×10^{-5}	3.3×10^{-4}
	20	23.2	5.3×10^{-4}	2.0×10^{-3}	5.4×10^{-4}	1.4×10^{-3}	1.2×10^{-3}	2.4×10^{-4}	0	3.7×10^{-4}
	50	8.5	2.0×10^{-4}	3.6×10^{-4}	$3\ \times10^{-4}$	1.3×10^{-4}	1.4×10^{-3}	4.7×10^{-5}	0	5.2×10^{-5}
Ga-Y [c]	5	29.8	1.1×10^{-3}	1.8×10^{-3}	5.2×10^{-4}	8.9×10^{-4}	2.1×10^{-3}	$9\ \times10^{-5}$	0	5.2×10^{-4}
	20	12.9	2.7×10^{-4}	2.9×10^{-4}	2.7×10^{-4}	1.1×10^{-4}	3.4×10^{-3}	6.2×10^{-5}	0	8.4×10^{-5}
	50	9.3	2.1×10^{-4}	1.9×10^{-4}	2.6×10^{-4}	4.6×10^{-5}	2.4×10^{-3}	1.6×10^{-5}	0	2.7×10^{-5}

[a] Total yield of benzene, toluene and xylene.

[b] Zeolite Y precalcined at 550 ° C.

[c] Zeolite Y exchanged with gallium nitrate, calcined at 550 ° C.

Bronsted acidity is essential. The presence of H^+ is therefore necessary for Ga to effectively dehydrogenate propane and the results of the current study are therefore in agreement with the recent observations of Meriaudeau and Naccache [14] that a synergy between Ga_2O_3 and H^+ is operative for the Ga doped ZSM-5 system with respect to propane activation.

Addition of Ga to zeolite Y does not appear to affect the overall activation of propane (fig. 3). However, it is apparent that for Ga-Y catalyst prepared by ion exchange and pre-calcinced at 550 ° C the initial yields of propene and hydrogen are respectively ca 2.5 times and 4 times higher than those for the corresponding Y zeolite (table 1); whereas the deactivated catalysts at 1 h reaction time show very similar yields. Similar results are also observed when Ga_2O_3 is mixed with pre-calcined zeolite Y. Hence, the formation of propene is significantly enhanced on Ga addition to H-Y confirming that a combination of Ga^{3+}/H^+ is necessary for selective propane activation to propene. While the yields of propene and H_2 are significantly enhanced on Ga addition, the yields of methane ethene and ethane are markedly decreased (table 1). This indicates that in the presence of Ga^{3+} the activation of propane is changed from the cracking mechanism observed for H-Y to a dehydrogenation pathway; this effect being achieved whether Ga^{3+} is added by cation exchange or by physically mixing Ga_2O_3 with zeolite Y.

The results of this study demonstrate that by using zeolite Y in place of ZSM-5 it is possible to examine the interaction of the gallium promoter with different acid forms. This approach therefore enables the role of the gallium as a catalyst promoter to be commented on. Addition of Ga to the Bronsted acid form of zeolite Y switches the propane activation mechanism from a cracking route to a dehydrogenation pathway; the presence of both Ga^{3+} and H^+ are necessary to achieve this effect. In addition, no evidence has been observed to indicate that Ga plays a significant role in the oligomerisation of the primary alkene products in the Ga-zeolite Y systems investigated. Further studies are now proceeding to determine the nature of the synergistic interaction of Ga^{3+} and H^+ in zeolite catalysts that gives rise to enhanced propane activation via the dehydrogenation pathway.

Acknowledgement

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