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Conversion of Propane Using H–ZSM-5 and Ga/H–ZSM-5 in the Presence of Co-fed Nitric Oxide, Oxygen, and Hydrogen

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The conversion of propane to propene and aromatic hydrocarbons has been studied using cofed NO, O_2, and H_2 to probe the reaction mechanism with H–ZSM-5 and Ga_2O_3/H–ZSM-5 physical mixtures as catalysts. NO co-feeding with H–ZSM-5 causes a decrease in the conversion of propane and in the yields of methane and aromatic products. These effects are reversible on the removal of NO, but there is a significant delay that is dependent on the duration of the NO co-feeding, indicating that the effects are due to poisoning of active sites. Although propane conversion decreases, NO does not affect the yield of propene. Similar effects are observed when NO is co-fed using Ga_2O_3/H–ZSM-5 as catalyst. O_2 co-feeding with H–ZSM-5 leads to an increase in propane conversion, propene yield, and deactivation rate, whereas, as observed with NO, the yields of methane and aromatic products are decreased. Co-feeding of excess H_2, which is a major product from the aromatization of propane, has very little effect on the conversion of propane over H–ZSM-5, although the selectivities to alkanes are increased. For Ga_2O_3/H–ZSM-5 physical mixtures containing 10–90% Ga_2O_3, H_2 co-feeding leads to a significant decrease in propane conversion and in the yield of aromatic products. For Ga_2O_3 alone, the co-feeding of H_2 gives a significant increase in propane conversion with only limited effects on the product selectivities. A series of experiments that use a physical mixture of Ga_2O_3 powder and pelleted H–ZSM-5 with and without co-fed H_2 in which the mixture is separated by sieving after reaction for 3 h at 600°C is described. The results are interpreted in terms of a mechanism in which propane is activated at the interface between the gallium oxide and the zeolite.

INTRODUCTION

In recent years, there has been considerable interest in the utilisation of C_1–C_4 alkanes as chemical feedstocks. Early work by Csiscery (1) showed that alkanes could be dehydrocyclodimerized using bifunctional catalysts, e.g., Pt supported on acidic alumina. These catalysts deactivated rapidly due to coke formation in addition to producing significant amounts of methane and ethane as by-products. In addition, zeolites were found to be active for alkane activation. Chen and Lucki (2) studied the disproportionation of alkanes using zeolites, e.g., mordenite, and Chen (3) and Cattanach (4, 5) demonstrated that ZSM-5 could be used to convert alkanes to aromatics. In particular, the use of zinc-exchanged ZSM-5 was described (5). Subsequently, research lead to the development of the Cyclar process for the aromatization of propane and butane (6). Gallium-modified H–ZSM-5 has been found to be the most effective catalyst for this reaction (7, 8).

There has been a marked interest in the mechanism of propane activation with zeolite catalysts, and it is generally recognized to involve a synergistic interaction between a gallium species and the zeolite. 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 of acid-catalyzed propane cracking to give methane and ethane (7). The initial activation of propane is slow relative to the secondary reaction of propene, and this factor complicates any reaction mechanism study.

The nature of the active site is, however, less well understood. Kazansky *et al.* (9), using infrared spectroscopy, indicated that Lewis acid sites located on the external surface of the zeolite crystallites could be important. Proposals by Mériaudeau and Naccache (10) and Bayense *et al.* (11) involved the activation of propane on a gallium phase to form the intermediate $C_3H_7^+$ which gives propene as the primary reaction product. Based on the effect of gallium addition to the zeolite on the product distribution (12), we have previously proposed that propane activation occurs at the interface between the gallium species and the zeolite acid site involving intermediates similar to those proposed for hydrocarbon cracking reactions (13). In this paper, we extend these mechanistic studies and discuss the effects of co-feeding nitric oxide, oxygen, and hydrogen as reactive probe molecules. This approach has previously be found to useful in the study of the methanol conversion reaction over H–ZSM-5 (14,

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15) and the Fischer–Tropsch reaction using Co/MnO catalysts (16, 17). The effect of hydrogen pretreatment has been extensively studied (18–23), and recent studies by Iglesia and co-workers (24–26) have specifically addressed the role of hydrogen transfer in the propane aromatization reaction. There have been a number of studies of propane aromatization in which co-fed oxygen has been investigated but conflicting effects have been reported, e.g., by Inui *et al.* (27) and Zatorski *et al.* (28). To date, there have been no detailed studies involving nitric oxide as a mechanistic probe, although there have been many studies of the reduction of nitric oxide by the hydrocarbons in the presence of oxygen (29–34), and there have been some initial reports concerning the reduction of NO by propane in the presence of excess oxygen over acidic zeolites (35) and alumina (36). The present study therefore represents the first comparative study of the use of reaction probe molecules to investigate the propane aromatization reaction and enables further details of the reaction mechanism to be described.

EXPERIMENTAL

Zeolite H–ZSM-5 was prepared by the method of Howden (37) with SiO_2/Al_2O_3 ratios of 35 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 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 prestabilized 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, hydrogen, nitric oxide/nitrogen, or oxygen/nitrogen.

RESULTS

Propane Conversion with H–ZSM-5, Ga_2O_3/H–ZSM-5, and Ga-Exchanged H–ZSM-5

Propane was reacted over H–ZSM-5 and gallium-modified H–ZSM-5, and the results are given in Table 1. It is apparent that increasing the SiO_2/Al_2O_3 ratio leads to a decrease in propane conversion and aromatics yield which is in line with the decreased number of acid sites. The addition of gallium either by ion exchange or by grinding Ga_2O_3 with H–ZSM-5 leads to an increase in propane conversion, an increase in the yield of aromatic products, and a decrease in the yield of methane; i.e., there is an increase in the yield of dehydrogenation products at the expense of cracked products. The two methods of gallium addition give similar effects, but the effect is more pronounced for the samples prepared by ion exchange; this is in agreement with previous studies (8) and has been attributed to the different dispersions of gallium achieved by the two methods. However, these experiments show that the effects of gallium promotion can be readily studied using physical mixtures and that this method enables a range of gallium levels to be investigated. In a second set of experiments, the reaction of propane was studied over separate beds of β-Ga_2O_3 and H–ZSM-5 separated by silica wool. Three different configurations were used:

(a) H–ZSM-5 (0.5 g);
(b) Ga_2O_3 (0.3 g) over H–ZSM-5 (0.5 g);
(c) H–ZSM-5 (0.5 g) over Ga_2O_3 (0.3 g).

The results of the initial catalyst performance (Table 2) indicate that the presence of Ga_2O_3 as a separate bed in

TABLE 1

Propane Aromatization over H–ZSM-5 and Ga/H–ZSM-5 Catalyst[a]

			10^{-2} Product yield (mol h^{-1})				
Sample	Ga (%)	Conversion (%)	CH_4	C_2H_4	C_2H_6	C_3H_6	Aromatics
H–ZSM-5 (35)	0	79.2	2.7	0.61	0.65	0.28	1.1
Ga_2O_3/H–ZSM-5 (35)	3.7	83.6	2.2	0.40	0.48	0.18	1.3
Ga–ZSM-5 (35)	3.4	86.1	1.8	0.32	0.49	0.17	1.5
H–ZSM-5 (280)	0	6.7	0.21	0.21	0.13	0.09	0
Ga_2O_3/H–ZSM-5 (280)	3.7	9.0	0.12	0.12	0.016	0.16	0.01
Ga–ZSM-5 (280)	2.1	13.8	0.18	0.16	0.043	0.21	0.05

[a] Reaction conditions: 600°C; propane WHSV = 4.7 h^{-1}.

TABLE 2

Propane Aromatization over Separate Beds of Ga_2O_3 and H-ZSM-5 at 550°C and Propane WHSV = 9.4 h^{-1}

				Selectivity (mol %)					
Top bed	Bottom bed	Pretreatment	Conversion (%)	H_2	CH_4	C_2H_4	C_2H_6	C_3H_6	Aromatics
—	H-HSM-5	None	35.2	10.8	40.1	13.3	16.3	9.0	4.3
Ga_2O_3	H-HSM-5	None	34.1	15.4	36.5	13.4	15.1	9.0	4.4
H-HSM-5	Ga_2O_3	None	35.0	12.9	39.6	12.7	15.8	9.1	4.5
Ga_2O_3	H-HSM-5	H_2	38.2	22.8	35.1	10.4	12.7	6.2	8.2
Ga_2O_3[a]	H-HSM-5	H_2	36.8	22.0	37.0	10.0	12.9	5.9	8.2

[a] Ga_2O_3 bed removed following H_2 pretreatment.

addition to the zeolite has no significant effect on the catalytic performance. Hydrogen pretreatment (15 h, 550°C) of configuration (b) leads to an increase in propane conversion and the selectivity to aromatic products (Table 2). In addition, for the hydrogen pretreatment of configuration (b) with subsequent removal of the Ga_2O_3 prior to the reaction of propane, although the conversion is similar to that of untreated H-ZSM-5, the selectivity to aromatic products is enhanced. Subsequent analysis of the zeolite indicated that some gallium had been transferred to the zeolite by the hydrogen pretreatment.

Effect of NO on Propane Conversion with H-ZSM-5

The effect of continuous co-feeding of NO on the aromatization 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.

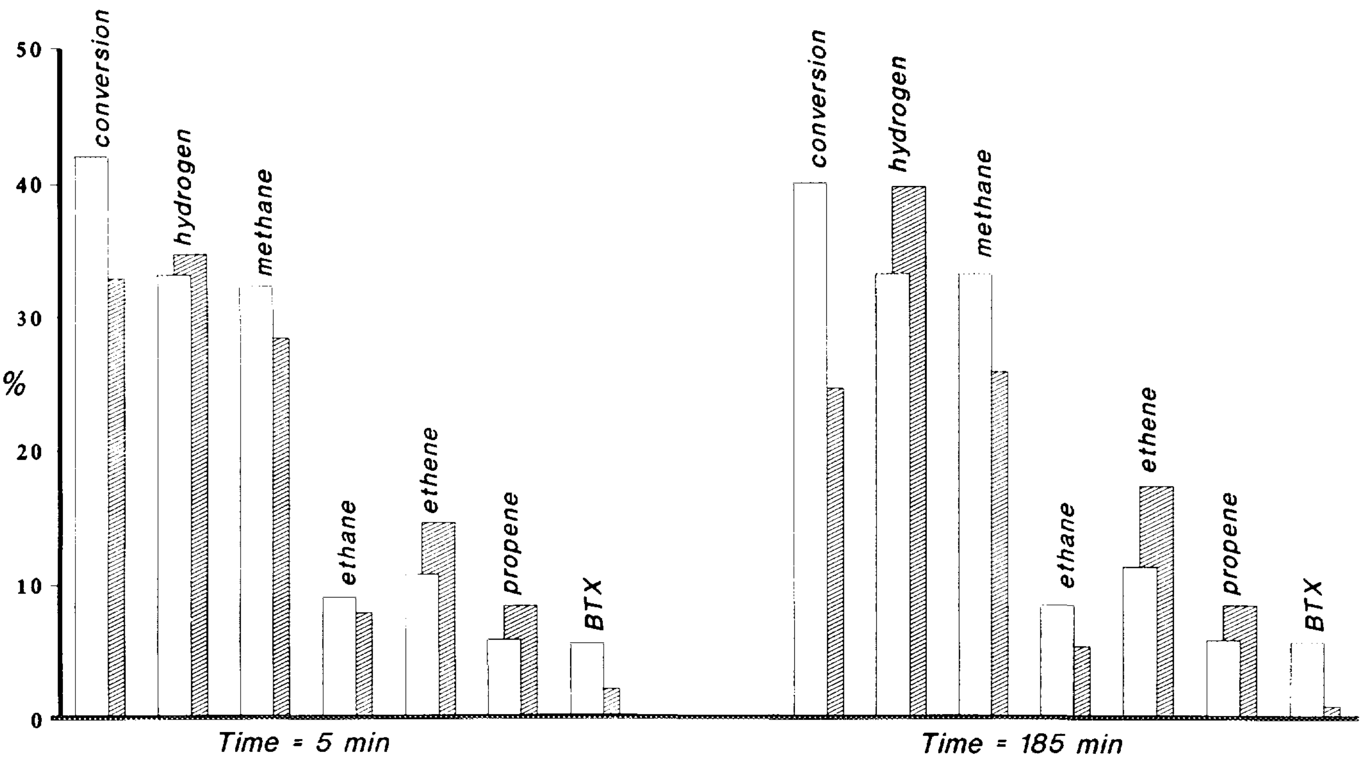


FIG. 1. Effect of NO co-feeding on propane aromatization over H-ZSM-5 at 550°C. NO co-feeding is represented by shaded areas.

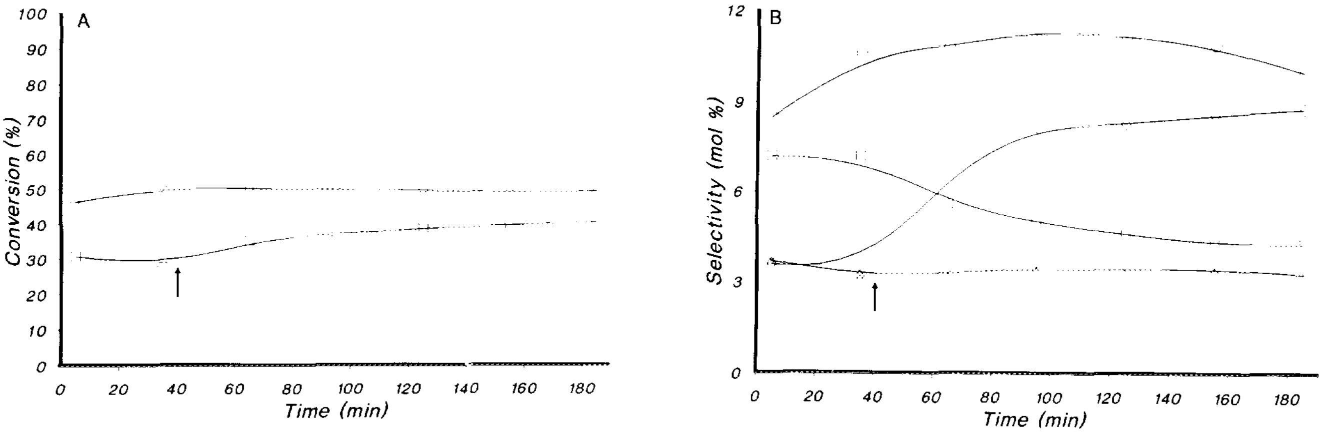


FIG. 2. Effect of NO cofeeding on propane aromatization over Ga_2O_3/H-ZSM-5 at 550°C. (A) Effect on conversion: ◇, without NO; □, with NO for the initial 40 min. (B) Effect on selectivity: ×, C_3H_6; □, C_3H_6 (NO); ○, aromatics; ◇, aromatics (NO). Arrow indicates the removal of co-fed NO from the reactants.

Effect of NO on Propane Aromatization with Ga_2O_3/H-ZSM-5

The effect of co-feeding NO on the aromatization of propane in the presence of N_2 diluent (propane : N_2 = 10 : 10) over Ga_2O_3/H-ZSM-5 physical mixture (5 mass% Ga_2O_3) at 550°C is shown in Fig. 2. In this experiment, NO was co-fed (propane : N_2 : NO = 10 : 9 : 1, total flowrate = 40 ml min^{-1}) for the first 40 min, after which time the NO co-feed was stopped and replaced with an equivalent amount of N_2. NO co-feeding leads to a significant loss of conversion when compared to the reaction in the absence of NO. After the NO is removed, the conversion slowly increases but does not attain the conversion observed for the NO-free reaction even following a further 85 min reaction. In addition, the presence of NO leads to an enhancement in propene selectivity and a decrease in the selectivities to aromatic products. As for the conversion, when the NO is removed the selectivities gradually approach those observed for the NO-free reaction. The effects of NO on propane aromatization over Ga_2O_3/H-ZSM-5 are therefore broadly similar to those observed with H-ZSM-5 alone.

The effect of introducing short NO pulses was investigated for the reaction of propane in the presence of N_2 diluent over a Ga_2O_3/H-ZSM-5 physical mixture at 600°C using the same reactant flow conditions used previously and a NO concentration during co-feeding of 5 mol% (Fig. 3). It is clear, as noted previously, that NO decreases propane conversion and that after each pulse the conversion does not attain the level of the NO-free reaction. It is also evident that the magnitude of the NO effect is dependent on the duration of the pulse. Similar results were obtained at 550°C. The relationship between the pulse duration and the decrease in propane conversion is shown in Fig. 4. The decrease in conversion is

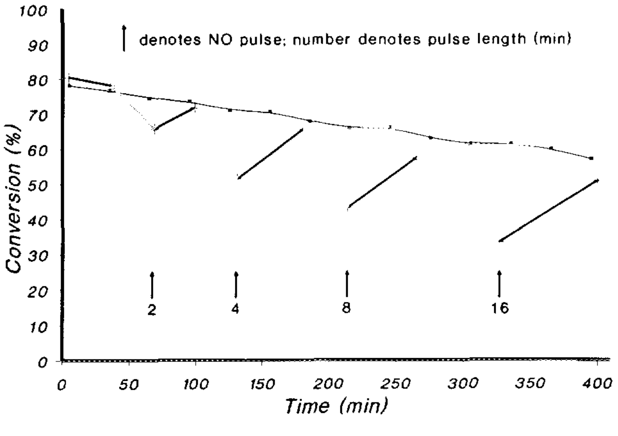


FIG. 3. Effect of NO pulses on propane conversion over Ga_2O_3/H-ZSM-5 at 600°C: ▣, without NO; +, with NO.

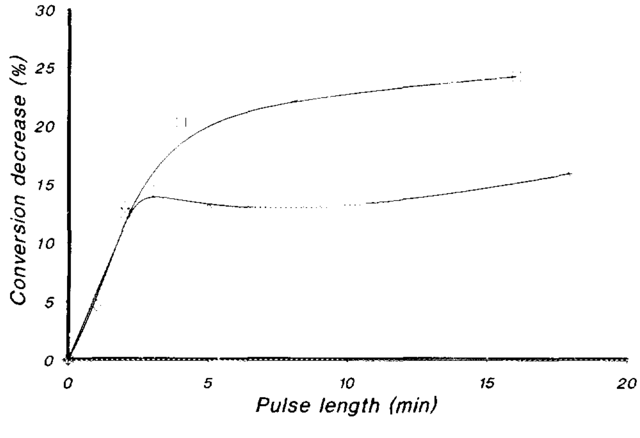


FIG. 4. Effect of NO pulse duration on propane conversion: ◇, 550°C; □, 600°C.

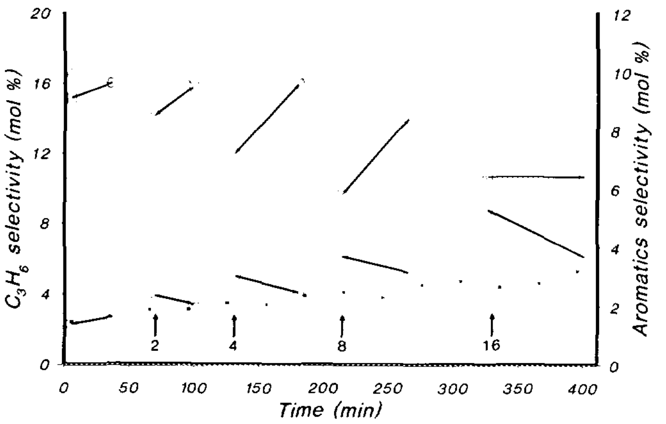


FIG. 5. Effect of NO pulses on propene and aromatic selectivity at 600°C: ▣, C_3H_6; , C_3H_6 (NO); ◇, aromatics; □, aromatics (NO).

defined as the difference between the conversion obtained immediately after the introduction of NO and the conversion obtained prior to the introduction of NO. It is apparent that short pulse durations are particularly effective. The effect of NO pulses on selectivity at 600°C is shown in Fig. 5, and similar results were obtained at 550°C. As noted previously, NO causes an increase in the propene selectivity while giving decreased selectivity to aromatic products, and these effects are also observed in the NO pulse experiments mirroring the conversion effects. In addition, it was found that the selectivity and conversion recovered after the NO pulse toward values characteristic of the NO-free reaction, but that the longer the duration of the pulse the longer the time required for the recovery to be observed.

Effect of O_2 on Propane Aromatization over H–ZSM-5

The effect of O_2 co-feeding (propane : N_2 : O_2 = 10 : 9 : 1) on propane aromatization at 550°C is shown in Fig. 6. 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 = 10 : 10). 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 led 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. 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.

Effect of H_2 on Propane Aromatization over Ga_2O_3, H–ZSM-5, and Ga_2O_3/H–ZSM-5

Hydrogen pretreatment of propane aromatization catalysts has been extensively studied (18–23), and more recently Iglesia and co-workers (24–26) have shown that hydrogen desorption plays a significant role in the overall kinetics of this process since hydrogen is one of the major reaction products. It is therefore of interest to investigate the effects of co-feeding excess hydrogen during the propane aromatization reaction. 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 (3.2%) is close to the experimental error limits for these results (conversion data are accurate to 1%). There are also minor effects on selectivity; 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 selectivity to propene 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

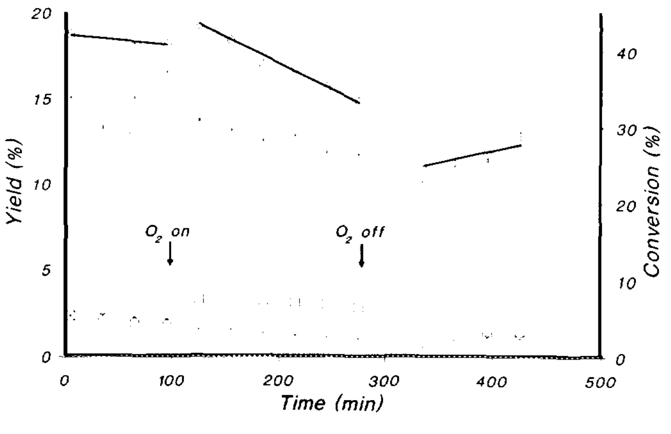


FIG. 6. Effect of O_2 co-feeding on propane aromatization over H–ZSM-5 at 550°C, O_2 co-feeding started at 95 min and stopped at 275 min time on line: ◇, conversion; +, H_2; , CH_4; □, C_3H_6; ×, aromatics.

TABLE 3

Propane Aromatization 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	22.4	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.

an increase in methane, ethane, and propene. The addition of 1% H–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 out using the same catalysts that had been pretreated in H_2 at 550°C for 30 min. The results, for the initial reaction period shown in Table 4, demonstrate similar effects to those observed for the nonpretreated materials when excess H_2 is co-fed. It is interesting to note that aromatic products are only observed as initial reaction products with Ga_2O_3 when the material has been pretreated with H_2 or H_2 is co-fed in excess.

A further set of experiments was conducted using a catalyst prepared by mixing 10% Ga_2O_3 powder with 90% H–ZSM-5 as pellets (0.5 mm particle size). The two materials were mixed using gentle agitation in a glass tube in the absence of grinding as had been used to prepare the physical mixtures used in the earlier experiments. In a series of experiments, this catalyst was separately reacted with propane in the presence of co-fed N_2 or H_2 (propane : co-feed = 1 : 4; total flowrate, 50 ml min^{-1}), and the results are shown in Fig. 7 and Table 5. It is apparent that the effects previously noted for H_2 co-feeding are observed; however, the effect on conversion is far more marked for the pelleted zeolite. After 185 min reac-

TABLE 4

Propane Aromatization over Hydrogen Pretreated 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
10	N_2	95.4	35.6	8.1	13.0	3.3	39.9
10	H_2	96.1	42.7	8.9	20.4	4.1	23.4
30	N_2	89.2	23.0	10.3	12.0	6.5	47.6
30	H_2	65.6	32.2	14.3	22.3	11.3	18.9
90	N_2	39.8	14.1	19.9	4.7	33.4	25.7
90	H_2	24.2	15.5	6.7	17.1	53.4	4.6
99	N_2	13.9	13.4	14.1	1.4	64.8	5.4
99	H_2	21.0	11.0	2.9	10.4	72.6	1.4
100	N_2	8.9	13.3	9.4	0.9	74.9	1.4
100	H_2	19.4	12.5	3.0	10.1	72.4	1.0

[a] Reaction conditions: 600°C; propane, 10 ml min^{-1}; co-feed, 40 ml min^{-1}; 0.5 g catalyst.
[b] Selectivity normalized excluding H_2.

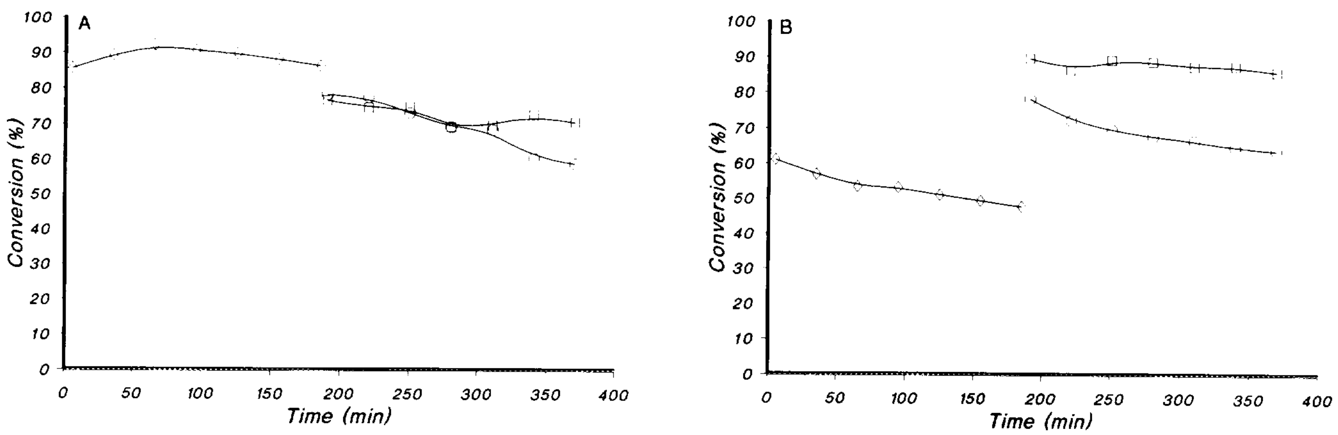


FIG. 7. Effect of H_2 co-feeding on propane aromatization over Ga_2O_3 (powder)/H–ZSM-5 (pellets) at 600°C. (A) Stage 1: ◇, reaction over Ga_2O_3/H–ZSM-5 with co-fed N_2; stage 2: reaction over H–ZSM-5 after sieving following reaction in stage 1: ○, N_2; □, H_2. (B) Stage 1; ◇, reaction over Ga_2O_3/H–ZSM-5 with co-fed H_2; stage 2: reaction over H–ZSM-5 after sieving following reaction in stage 1: □, N_2; +, H_2.

tion 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 resulted 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. 7) 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 5), 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. 7. It is clear that following the removal of the Ga_2O_3 powder 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

TABLE 5

Propane Aromatization 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.

N_2 co-feed. Such behavior is characteristic of Ga_2O_3/H–ZSM-5 mixtures (Table 3) and the selectivity data are also consistent with this observation.

DISCUSSION

Comments on the Effect of Co-feeding of NO, O_2, and H_2

The co-feeding of NO during the propane aromatization reaction leads to a number of effects of both H–ZSM-5 and Ga_2O_3/H–ZSM-5 that are of mechanistic significance. First, NO co-feeding either continuously or as a pulse leads to a rapid decrease in conversion together with an increase in propene selectivity. Inspection of the data for all conditions examined indicates that the yield of propene is unchanged by the presence of NO, prior to the subsequent deactivation that is also initiated by NO. For example, at 550°C over H–ZSM-5 (Fig. 1) the propene yield, as defined by the simple product of conversion and selectivity, is *ca.* 2.5% in the presence and absence of NO, and for Ga_2O_3/H–ZSM-5 at the same conditions the propene yield is *ca.* 2.0% in the presence and absence of NO. It is therefore apparent that NO has no effect on the activation of propane to form propene. In addition this effect indicates that the formation of propene from propane is via an equilibrium-controlled process. However, calculations based on thermodynamic data (38) and reactor exit analysis for propane, propene, and hydrogen indicate that the concentration of propene is higher than that expected. These observations are in agreement with the recent studies by Iglesia *et al.* (24) using isotopic methods which have also indicated that this step is in equilibrium. They concluded that the higher than expected propene selectivity was due to hydrogen exerting a virtual pressure on the surface due to the recombination of H monatomic species being rate-limiting. In this way, the gas-phase hydrogen concentration has a lesser effect on the equilibrium, and this concept has been previously used by Temkin and Pyzhev (39) to explain a similar situation for the effect of nitrogen pressure on the ammonia decomposition reaction over iron catalysts for which the recombination of N atoms is rate-limiting.

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 observed for the selectivity data. This indicates that NO is not acting as a radical scavenger in the propane aromatization reaction, since if this were the case the recovery in catalytic performance would also have been immediate, as is observed for methane coupling (40) which is generally agreed to involve radical intermediates. Hence, it can be concluded that the intermediates in the propane aromatization 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 (14, 15). 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 Brønsted 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. Previous studies (35, 36) have shown that NO can be reduced in the presence of propane and oxygen over zeolites and other acidic oxides, demonstrating that such a proposal is feasible. In addition, recent studies (41) have shown that NO reacts with hydrocarbons over zeolite catalysts to form a stable nitro species that remains adsorbed at elevated temperatures and requires the presence of oxygen for it to be decomposed. It is considered that a similar reaction occurs for NO in the propane aromatization reaction which, in the absence of oxygen, remains adsorbed at the acid site, thereby poisoning the catalyst. Further evidence to support this has been provided by the studies of Yogo *et al.* (42, 43) which have shown that the selective reduction of NO by hydrocarbons, including propane, over Ga–ZSM-5 is not affected by oxygen in the concentration range 2–10%. However, the presence of oxygen was found to be crucial, since in the absence of oxygen no NO reduction occurred.

Co-feeding O_2 during the propane aromatization 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 propene being equilibrium-controlled with O_2 reacting with H_2, thereby enabling increased propane conversion. The addition of O_2 also causes significant deactivation to occur, possibly via coke formed by the polymerization of hydrocarbon oxidation products. However, the deactivation is partially reversed on removal of O_2, and the product yields recover toward 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-catalyzed cracking, oligomerization, and aromatization reactions, whereas NO does not affect the selective activation of propane to propene and O_2 enhances this reaction by removing H_2.

As described previously, 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 there is 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 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.* (24). 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 Brønsted acid sites of H–ZSM-5 and that the zeolite possesses hydrogenating activity (44).

Comments on the Nature of the Active Site and the Reaction Mechanism of Propene Activation

For the propane aromatization reaction 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 Brønsted acid bridging hydroxyl groups. Propane activation can be considered to occur in either of three ways:

(a) abstraction of H · to form $C_3H_7\cdot$;
(b) addition of H^+ to form $C_3H_9^+$;
(c) abstraction of H^- to form $C_3H_7^+$.

The abstraction of a hydrogen atom to form a radical intermediate 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 (Fig. 8). 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 is therefore possible that activation of the propane by the Brønsted acid sites could lead to the formation of both the cracked and the selective products.

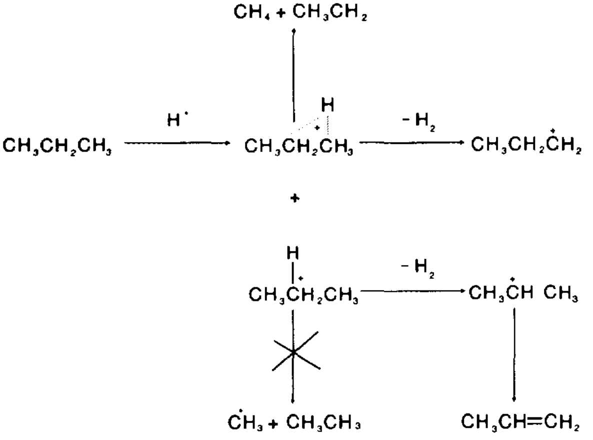


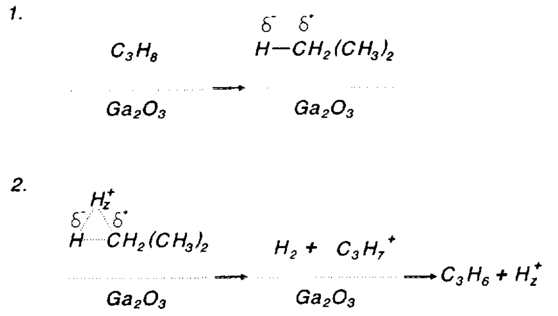
FIG. 8. Propane activation via protonation.

When the gallium oxide is added to the zeolite it is possible that these zeolite-catalyzed reactions still occur at unmodified Brønsted acid sites. However, the catalyst activity and aromatic yield is so markedly promoted that it is apparent that new active sites are now involved. The experiments carried out in this study have shown that the initial activity of the Ga_2O_3/H–ZSM-5 physical mixtures is markedly different from those of the oxide and the zeolite separately. This represents an example of contact synergy which has been well documented previously for oxide catalysts (45, 46). It is therefore apparent that new high-activity sites are present before any substantial modification of the catalyst has occurred. The activity and performance of these catalyst 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. This contact synergy is particularly exemplified by the addition of 1% H–ZSM-5 to Ga_2O_3 which results in a dramatic increase in propane conversion and aromatic yield. In addition, the experiments with the physical mixture of the powdered Ga_2O_3 and pelleted zeolite indicate that these sites can be formed 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 of interest to consider the intermediates that could be involved in possibility (b). The experiments involving separate beds of the oxide and the zeolite indicate that the reaction simply does not involve the initial dehydrogenation of propane to propene on the gallium oxide,



H_z^+ denotes proton associated with the zeolite

FIG. 9. Proposed mechanism for propane activation on Ga_2O_3/H-ZSM-5.

since a separate bed of the oxide upstream of the zeolite did not affect the catalytic performance of the zeolite. It is clear that the two components must be in close proximity. As discussed previously, propane can be activated to form three possible intermediates $(C_3H_7 \cdot C_3H_9^+, C_3H_7^+)$. Again the possibility of a radical intermediate being involved can be excluded on the basis of the NO cofeeding results. Propane activation via H^+ addition to form $C_3H_9^+$ would be expected to lead to the formation of methane and C_2 hydrocarbons, as shown in Fig. 8. A number of previous studies (10, 11) have proposed that the gallium phase acts as a H^- acceptor from propane to form the $C_3H_7^+$ intermediate which then reacts with the zeolite to form propene. The formation of $C_3H_7^+$ from propane requires the heterolytic cleavage of a strong C–H bond with a high enthalpy of reaction (47). Such a step would be anticipated to be rate-limiting and lead to only a low rate of propane activation via this route in comparison to activation by H^+ addition. In addition, it is possible that the reactive $C_3H_7^+$ species could react with the co-fed NO or other co-fed gases which would significantly affect propene formation, but this is not observed. Based on this discussion the transfer of an intermediate between the catalyst components is not considered to be probable (i.e., pathway (b)). We propose that the propane is activated at the interface between the Ga_2O_3 and the zeolite Brønsted acid site (i.e., pathway (a)). The initial process is the polarization of the C–H bond by the Ga_2O_3. Studies using infrared spectroscopy have indicated that C–H bond polarization can occur over this oxide (9), which gives support to this proposal. Subsequently, the polarized C–H bond is cleaved by interaction with the zeolite Brønsted acid site (Fig. 9) in a reaction that is analogous to that considered to occur in propene cracking over zeolite catalysts (13). Hence, the role of the gallium phase is to enable C–H bond polarization to be induced so that it is susceptible to reaction with the zeolite acid sites. In this mechanism, the zeolite and the gallium oxide are considered to act in concert at an active site that is located at the interface between these two phases.

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