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Methanol to hydrocarbons: enhanced aromatic formation using composite group 13 oxide/H-ZSM-5 catalysts

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The conversion of methanol to hydrocarbons using composite catalysts comprising physical mixtures of the zeolite H-ZSM-5 with group 13 oxides (γ-Al_2O_3, β-Ga_2O_3, In_2O_3, Tl_2O_3) is reported and discussed. The addition of β-Ga_2O_3 at 400 °C gives a marked enhancement in the yield of C_8 and C_9 aromatic compounds, whereas the addition of γ-Al_2O_3 has no effect and both the In_2O_3/H-ZSM-5 and Tl_2O_3/H-ZSM-5 are inactive. At 300 °C, a marked enhancement in the yield of aromatic hydrocarbons is observed for β-Ga_2O_3 and In_2O_3, and a less marked enhancement is observed with Tl_2O_3 and γ-Al_2O_3. In particular, the addition of In_2O_3 to H-ZSM-5 as a simple physical mixture gives a significant enhancement in catalyst activity at 300 °C. The effect of the Si : Al atomic ratio of H-ZSM-5 is also investigated for the β-Ga_2O_3/H-ZSM-5 composite catalysts and the enhancement in aromatic yield is observed with all the ratios investigated but the optimal β-Ga_2O_3/H-ZSM-5 ratio is dependent upon the Si : Al ratio. Pretreatment or co-feeding of hydrogen decreases the yield of the aromatic products. The results are explained in terms of an active site formed by the interaction between the oxide and the zeolite.

KEY WORDS: promotion in heterogeneous catalysis; methanol conversion; aromatic hydrocarbon synthesis; H-ZSM-5; group 13 oxides; β-$Ca\theta_2O_3$/H-ZSM-5 composite catalysts.

1. Introduction

The conversion of methanol to hydrocarbons represents an exceptionally well-studied reaction since the reaction was initially reported by Chang and Silvestri in 1977 [1]. Chang and Silvestri noted that the zeolite H-ZSM-5 was particularly effective for the conversion of methanol to C_5–C_{11} hydrocarbons and, furthermore, the catalyst activity could persist for many days. Oxides, other than zeolites, have also been investigated, *e.g.*, WO_3/γ-Al_2O_3 [2] but, in general, these oxides do not exhibit sufficient acidity and methane dominates as a reaction product rather than C_5–C_{11} hydrocarbons. In view of this, zeolites have been well studied and a broad range of zeolites have been studied for the methanol to hydrocarbons reaction, including zeolite Y [3], zeolite β [4], mordenite [5] and clinoptilolite [6]. Other non-zeolite microporous materials have been evaluated, *e.g.*, $AlPO_4$-5, MeAPO-5 [7] and SAPO-34 [8], especially as these tend to catalyze the formation of C_2–C_4 alkenes as the main products.

The extensive literature concerning the methanol to hydrocarbons reaction, particularly for the formation of light alkenes, has been reviewed by Stöcker [9]. Previously, a number of reviews have addressed the formation of gasoline-range hydrocarbons from methanol [10–12].

Since 1977, many modifications of the zeolite catalysts have been investigated. In particular, the substitution of the tetrahedral framework atoms (Al, Si) by other atoms (*e.g.*, Ga, Fe, B) have been extensively studied and this literature has been reviewed by Stöcker [9]. In all these previous studies it is surprising that the use of composite catalysts, in which an oxide and a zeolite are mixed together as a simple physical mixture, have not until recently [13–15] been investigated for the methanol to hydrocarbons reaction. This is even more surprising when these composite catalysts (*e.g.*, physical mixtures of β-Ga_2O_3 and H-ZSM-5) have been extensively studied for the aromatization of propane [16–18]. In our recent studies [14,15], we have shown that the addition of β-Ga_2O_3 to H-ZSM-5 (Si : Al atomic ratio = 80) significantly enhances the formation of C_8 and C_9 aromatics for methanol conversion. We also showed [15] that an effect can be observed for the addition of β-Ga_2O_3 to WO_3 but, in this case, the enhanced reactivity was for methane formation. In this paper, we extend the study of composite catalysts to materials comprising physical mixtures of H-ZSM-5 with group 13 oxides other than β-Ga_2O_3 and show that the effect can also be observed with In_2O_3, but the reaction temperature required is significantly lower.

2. Experimental

Zeolite H-ZSM-5 (Si : Al ratios = 80, 50, 30) were obtained as commercial samples from PQ Corporation. Gallium oxide (β-Ga_2O_3), indium oxide (In_2O_3), thallium oxide (Tl_2O_3) and alumina (γ-Al_2O_3) were obtained from

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Aldrich. These mixtures were used individually as coarse particles (0.6–1.0 mm) prepared by pelleting the powder, crushing the pellets and sieving to obtain the correct size fraction. In addition, physical mixtures of the oxides and the zeolite were prepared using two methods: (a) by crushing the two powders together (1 : 1 by weight) prior to forming particles (0.6–1.0 mm) as described above, and (b) by mixing the two powders together (1 : 1 by weight) without crushing, using a rotating sample tube prior to forming particles (0.6–1.0 mm) as described above.

The catalysts were tested for the methanol conversion reaction using a standard tubular glass laboratory microreactor. Methanol was fed to the reactor using a calibrated syringe pump, and all data presented are for a standard feedrate (WHSV = $1.3\,h^{-1}$). The methanol was mixed with a helium diluent prior to vaporization. Catalyst samples (typically 0.2–0.3 g) were contained in the heated zone of a tubular glass microreactor (9 mm i.d.) and all lines to and from the reactor were heated to avoid condensation of the reactants and/or products. Product analysis was carried out using gas chromatography using a flame ionization detector with a Poropac Q column (2 m × 3 mm). Blank reactions in the absence of the catalysts, but using a reactor packed with boron nitride or glass heads, showed no activity for the methanol conversion reaction at the reaction conditions evaluated.

3. Results and discussion

3.1. *Methanol conversion over group 13 oxide/H-ZSM-5 (Si : Al = 80) catalysts*

H-ZSM-5 (Si : Al = 80) and the group 13 oxides were separately reacted with methanol at 300 and 400 °C and the results are shown in tables 1 and 2. At 300 °C, all the materials gave only very low conversion to hydrocarbons, although γ-Al_2O_3 and β-Ga_2O_3 were active for the conversion of methanol to dimethyl ether. It is interesting to note that this sample of H-ZSM-5 (Si : Al = 80) was relatively inactive at these temperatures and reagent flow rate and this low level of activity persisted for 870 min. This is considered to be due to the high Si : Al ratio of this sample of H-ZSM-5. At 400 °C, H-ZSM-5 (Si : Al = 80) was now an effective catalyst (table 1) but all the other oxides gave only very low levels of conversion. Again, γ-Al_2O_3 and β-Ga_2O_3 gave some conversion of methanol to dimethyl ether.

A series of experiments were conducted at 400 °C in which the group 13 oxides were mixed with H-ZSM-5 and used as catalysts for the methanol conversion reaction. The composite catalyst comprising γ-Al_2O_3/H-ZSM-5 did not show any difference for the reaction with H-ZSM-5 alone (table 1). As noted previously [14,15], the addition of β-Ga_2O_3 to H-ZSM-5 (Si : Al = 80) in a physical mixture (1 : 1 by weight) significantly enhances the formation of aromatic hydrocarbons at 400 °C (table 1). It is apparent that the aromatic compounds are formed at the expense of light alkenes. In particular, C_8 and C_9 aromatic hydrocarbons are formed by the β-Ga_2O_3/H-ZSM-5 catalyst and it is considered that these are formed by the dimerization and trimerization of the light alkenes formed from methanol on the H-ZSM-5 catalysts. In separate experiments reported elsewhere [15], it was found that the addition of β-Ga_2O_3 did not enhance the xylene isomerization/alkylation activity, nor did the β-Ga_2O_3/H-ZSM-5 activate long-chain alkanes (*e.g.*, heptane) to form aromatics at 400 °C under these reaction conditions. The effect appears to be due to contact synergy

Table 1
Methanol conversion over H-ZSM-5 and group 13 oxide/H-ZSM-5 (Si : Al = 80) composite catalysts at 400 °C [a]

Catalyst	Reaction time (min)	Methanol conversion (%)	Product selectivity (%) [b]										Aromatic hydrocarbon yield (%)
			CH_4	C_2	C_3	C_4	C_5	C_{6+}	C_6H_6	C_7H_8	C_8H_{10}	C_9H_{12}	
H-ZSM-5 [c]	30 [f]	100	0.1	3.8	39.1	27.5	6.6	11.5	4.5	1.3	3.9	1.7	11.4
γ-Al_2O_3 [c,d]	30 [f]	3.9 [f]	97.9	0.7	1.4	–	–	–	–	–	–	–	0
β-Ga_2O_3 [c,d]	30	<0.5	tr	tr	tr	–	–	–	–	–	–	–	0
In_2O_3 [c]	30	<0.5	tr	–	–	–	–	–	–	–	–	–	0
Tl_2O_3 [c]	30	<0.5	tr	–	–	–	–	–	–	–	–	–	0
γ-Al_2O_3/H-ZSM-5 [c]	30	100	0.5	4.6	38.2	25.4	12.2	9.3	4.1	1.1	2.9	1.8	9.8
	870	100	0.7	4.3	40.9	26.3	11.6	7.5	3.6	1.2	3.6	1.5	9.8
β-Ga_2O_3/H-ZSM-5 [e]	30	100	0.3	13.6	22.5	9.9	3.9	3.7	1.6	2.9	14.9	26.8	46.1
	870	100	0.9	13.7	26.0	16.0	4.9	4.7	2.2	2.7	12.1	16.9	33.8
In_2O_3/H-ZSM-5 [e]	30	<1.0	tr	tr	tr	tr	tr	–	–	–	–	–	0
Tl_2O_3/H-ZSM-5 [e]	30	<0.5	tr	tr	tr	tr	tr	–	–	–	–	–	0

[a] Reaction conditions: 400 °C, WHSV = $1.3\,h^{-1}$, helium diluent $60\,ml\,min^{-1}$.

[b] Selectivities for C_2–C_{6+} hydrocarbons are quoted as alkene and alkane. Alkene/alkane ratio typically 50 : 1, tr = trace.

[c] Zeolite or oxide (0.125 g) particles (0.6–1 mm) mixed with glass beads as diluent (0.125 g).

[d] Some conversion to CH_3CHO_3 is also observed.

[e] H-ZSM-5 (0.125 g) and the oxide (0.125 g) crushed together, and pelleted, crushed, sieved to give particles (0.6–1.0 mm).

[f] Catalyst activity stable for 870 min, data for 30 min are representative of 30–870 min period.

Table 2
Methanol conversion over H-ZSM-5 and group 13 oxide/H-ZSM-5 (Si : Al = 80) composite catalysis at 300 °C[a]

Catalyst	Reaction time (min)	Methanol conversion (%)		Product selectivity (%)[b]										Aromatic hydrocarbon yield (%)
		Hydrocarbons	CH_3OCH_3	CH_4	C_2	C_3	C_4	C_5	C_{6+}	C_6H_6	C_7H_8	C_8H_{10}	C_9H_{12}	
H-ZSM-5[c]	30[f]	<0.5	68.0	tr	tr	tr	–	–	–	–	–	–	–	nd
γ-Al_2O_3[c]	30[f]	<0.1	72.0	tr	tr	tr	–	–	–	–	–	–	–	nd
β-Ga_2O_3[c]	30	0.1	53.0	tr	–	–	–	–	–	–	–	–	–	nd
In_2O_3[c]	30	<0.1	tr	tr	–	–	–	–	–	–	–	–	–	nd
Tl_2O_3[c]	30	<0.1	tr	tr	–	–	–	–	–	–	–	–	–	nd
γ-Al_2O_3/H-ZSM-5[d]	870[e]	2.8	68.3	0.6	15.9	52.1	11.4	6.2	13.7	tr	tr	tr	tr	tr
β-Ga_2O_3/H-ZSM-5[d]	870[e]	3.6	65.0	0.3	29.4	38.1	6.6	34.0	14.7	tr	tr	4.5	3.0	7.5
In_2O_3/H-ZSM-5[d]	30	30.8	sh	0.4	17.1	29.3	15.1	8.3	20.2	0.5	1.1	3.7	4.5	9.8
	870	6.1	sh	0.6	18.0	34.0	15.2	6.6	14.2	0.3	0.4	5.9	4.2	10.8
In_2O_3/H-ZSM-5[f]	30	7.5	65.0	0.5	19.6	33.0	7.5	8.6	23.5	tr	tr	2.9	4.1	7.0
	870	6.8	63.3	0.4	19.8	39.4	10.1	5.4	19.4	tr	0.9	3.3	1.3	5.5
Tl_2O_3/H-ZSM-5[d]	30	0.7	0	0.7	19.2	31.2	20.5	6.6	9.8	tr	0.7	8.7	3.0	12.5
	870	0	0	–	–	–	–	–	–	–	–	–	–	–

[a] Reaction conditions: 300 °C, WHSV = $1.3\,h^{-1}$, helium diluent $60\,ml\,min^{-1}$.

[b] Selectivities for C_2–C_6 hydrocarbons are quoted as alkene and alkane. Alkene/alkane ratio typically 50 : 1, tr = trace, nd = not detected, sh = shoulder presence of CH_3OCH_3 with the CH_3OH.

[c] Zeolite or oxide (0.125 g) particles (0.6–1.0 mm) mixed with glass heads as diluent (0.125 g).

[d] H-ZSM-5 (0.125 g) and the oxide (0.125 g) crushed together lightly in a pestle and mortar, pelleted, crushed, sieved to give particles (0.6–1.0 mm).

[e] Conversion stable throughout 870 min experiment.

[f] Catalyst activity stable for 870 min, data at 30 min are representative of 30–870 min period.

in which new active sites are formed at the junction between the crystallites of the two components. In our preliminary communication [14], we have demonstrated that these sites can be formed reversibly.

At 400 °C, the addition of In_2O_3 or Tl_2O_3 as a physical mixture resulted in a total and immediate loss of catalyst activity. Examination of the zeolite by X-ray powder diffraction showed that the zeolite structure was not affected and so the effect is not due to loss of zeolite crystallinity. The catalysts did show some initial activity but the catalysts rapidly deactivated due to the formation of carbonaceous material. We considered this indicated that these catalysts could be very active for the methanol conversion reaction, but the rate of deactivation was too rapid under these reaction conditions to observe the catalyst activity and the nature of the reaction products.

In view of this, the experiments were repeated at 300 °C and the results are given in table 2. Under the reaction conditions selected, the zeolite H-ZSM-5 alone was relatively inactive throughout the test period of 870 min. In particular, no aromatic hydrocarbons were observed, and only traces of methane and C_2–C_4 hydrocarbons were formed. Now all the group 13 oxides enhance the catalyst activity significantly when used as physical mixtures with H-ZSM-5. The most marked effects were observed with β-Ga_2O_3 and In_2O_3. The In_2O_3/H-ZSM-5 composite catalyst, prepared by crushing the two powders together, gives an initial conversion of methanol, at these conditions, which is about two orders of magnitude higher than the H-ZSM-5 catalyst alone (table 2). However, the catalyst prepared in this way is not stable and the conversion declines during the catalyst test period of 870 min. The In_2O_3/H-ZSM-5 composite catalyst, prepared by mixing the powders without crushing, gives stable activity throughout the reaction time, but exhibits lower activity (table 2). The addition of β-Ga_2O_3 also gives a significant enhancement in the conversion of methanol. At 300 °C, the addition of Tl_2O_3 also showed some initial activity but this catalyst rapidly deactivated. The effect of deactivation on catalyst performance is shown for the γ-Al_2O_3/H-ZSM-5, β-Ga_2O_3/H-ZSM-5, In_2O_3/H-ZSM-5 and H-ZSM-5 catalysts in figure 1. It is clear that the effect of enhanced catalyst activity and for the formation of hydrocarbons is observed for a significant time period.

A set of experiments were carried out with the β-Ga_2O_3/H-ZSM-5 (Si : Al = 80) composite catalysts to investigate the effect of intermediate reaction temperatures, between 300 and 400 °C, on the yield of aromatic hydrocarbons and the results are shown in figure 2. It is apparent that both the conversion and aromatic hydrocarbon yield increase with increasing reaction temperatures.

In a further set of experiments, the degree of mixing of In_2O_3 and H-ZSM-5 (Si : Al = 80) was investigated at 300 and 350 °C and the results are shown in tables 3 and 4. At 300 °C, a simple physical mixture of In_2O_3 and H-ZSM-5 particles prepared without crushing was found to be relatively inactive (experiment 5). Two physical mixtures containing In_2O_3/H-ZSM-5 in 1 : 3 and 1 : 1 weight ratios (experiments 2 and 3) demonstrated rapid deactivation with reaction time. The best results from In_2O_3 at 300 °C are obtained when the oxide and the zeolite are not crushed together, but are mixed with gentle agitation prior to pelleting and sieving (experiment 4).

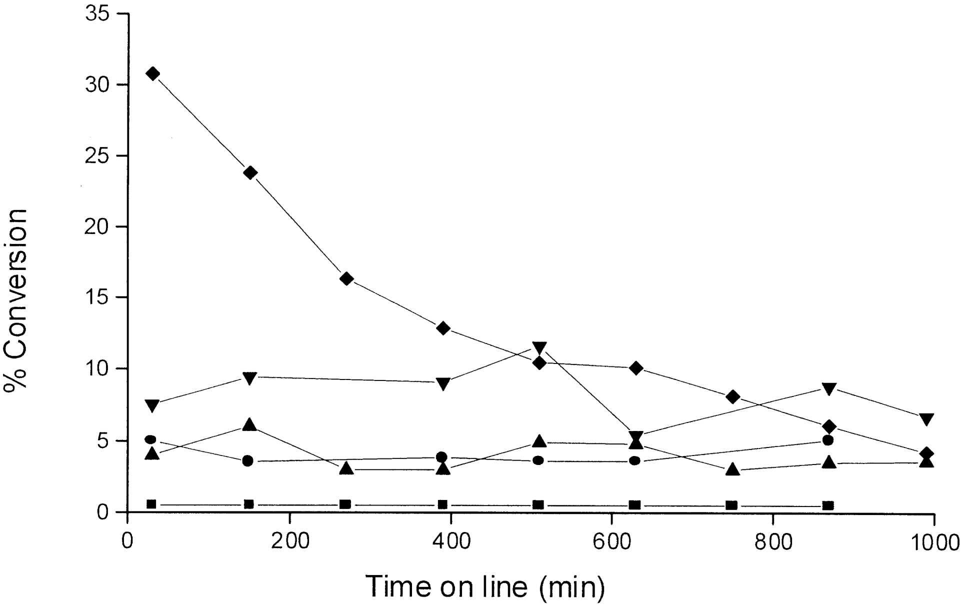

Figure 1. Methanol conversion (300 °C, WHSV = 1.3 h^{-1}, helium diluent 60 ml min^{-1}) over H-ZSM-5 and composite catalysts. ◆, In$_2$O$_3$/H-ZSM-5 crushed together before pelleting; ▼ In$_2$O$_3$/H-ZSM-5 mixed together without crushing; ●, β-Ga$_2$O$_3$/H-ZSM-5; ▲, γ-Al$_2$O$_3$-H-ZSM-5; ■, H-ZSM-5. Reaction conditions: 300 °C, WHSV = 1.3 h^{-1} helium diluent 60 ml min^{-1}.

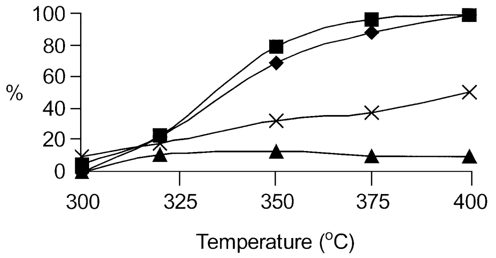

Figure 2. Methanol conversion (WHSV = 1.3 h^{-1}, helium diluent 60 ml min^{-1}) over β-Ga$_2$O$_3$/H-ZSM-5 (Si : Al = 80) and H-ZSM-5. Key: β-Ga$_2$O$_3$/H-ZSM-5: ■, methanol conversion, ×, aromatic hydrocarbon yield; H-ZSM-5: ◆, methanol conversion, ▲, aromatic hydrocarbon yield.

In this case, the catalyst activity is stable and enhanced aromatic hydrocarbon selectivity is observed throughout the 870 min experiment. It is clear that the method of preparation of these composite mixtures requires careful optimization to observe these interesting effects.

3.2. *Effect of Si : Al ratios on β-Ga$_2$O$_3$/H-ZSM-5 catalysts*

Three H-ZSM-5 zeolites with different Si : Al ratios (30, 50, 80) were tested for the methanol conversion at 400 °C with and without the addition of β-Ga$_2$O$_3$ as a physical mixture (1 : 1 by mass). The results are given in

Table 3
Methanol conversion over H-ZSM-5, In$_2$O$_3$[c]and In$_2$O$_3$[c]/H-ZSM-5 catalysts at 30 °C[a]

Experiment	Catalyst	Reaction time (min)	Methanol conversion (%)		Product selectivity (%)[b]										Aromatic hydrocarbon selectivity (%)
			Hydrocarbons	CH_3OCH_3	CH_4	C_2	C_3	C_4	C_5	C_{6+}	C_6H_6	C_7H_8	C_8H_{10}	C_9H_{12}	
1	H-ZSM-5[c]	30	<0.5	68.0	tr	tr	tr	–	–	–	–	–	–	–	0
2	In$_2$O$_3$/H-ZSM-5[d]	30	30.8	sh	0.4	17.1	29.3	15.1	8.3	20.2	0.5	1.1	3.7	4.5	9.8
		870	6.1	sh	0.6	18.0	34.0	15.2	6.6	14.2	0.3	0.4	5.9	4.2	10.8
3	In$_2$O$_3$/H-ZSM-5[e]	30	7.5	65.0	0.5	19.6	33.0	7.5	8.6	23.5	tr	tr	2.9	4.1	7.0
		870	6.8	63.3	0.4	19.8	39.4	10.1	5.4	19.4	tr	0.9	3.3	1.3	5.5
4	In$_2$O$_3$/H-ZSM-5[f]	30	11.4	59.6	0.4	20.7	32.1	7.9	8.4	20.4	tr	1.9	3.8	4.23	10.1
		870	13.2	55.2	0.4	19.2	38.4	11.2	6.4	13.0	1.4	2.6	3.1	4.5	11.5
5	In$_2$O$_3$/H-ZSM-5[g]	30	<1.0	N/A	tr	tr	tr	tr	tr	–	–	–	–	–	0

[a] Reaction conditions: 300 °C, WHSV = 1.3 h^{-1}, helium diluent 60 ml min^{-1}.
[b] Selectivities for C$_2$–C$_{6+}$ hydrocarbons are quoted as alkene and alkane. tr = trace.
[c] H-ZSM-5 (0.125 g, Si : Al = 80) particles (0.6–1 mm) mixed with glass beads as diluent (0.125 g).
[d] Physical mixture of β-In$_2$O$_3$ with H-ZSM-5 crushed 1 : 3 weight ratio (0.25 g, pellets, 0.6–1.0 mm).
[e] Physical mixture of β-In$_2$O$_3$ powder (0.125 g) and H-ZSM-5 powder (0.125 g, pressed pellets, 0.6–1.0 mm).
[f] Physical mixture of β-In$_2$O$_3$ with H-ZSM-5 crushed 1 : 3 weight ratio (0.125 g, pellets, 0.6–1.0 mm).
[g] Physical mixture of β-In$_2$O$_3$ (0.124 g, pellets, 0.25–3.0 mm) with H-ZSM-5 (0.125 g, pellets, 0.6–1.0 mm); not crushed.

Table 4
Methanol conversion over H-ZSM-5, In_2O_3 and In_2O_3/H-ZSM-5 catalysts at 350 °C[a]

Catalyst	Reaction time (min)	Methanol conversion to hydrocarbons (%)	Product selectivity (%)[b]										Aromatic hydrocarbon yield (%)
			CH_4	C_2	C_3	C_4	C_5	C_{6+}	C_6H_6	C_7H_8	C_8H_{10}	C_9H_{12}	
H-ZSM-V[c]	30	69.7	0.2	10.5	30.6	19.1	14.1	12.6	3.7	1.3	4.6	3.3	12.9
In_2O_3/H-ZSM-5[d]	30	100	0.2	4.3	30.3	26.4	12.3	12.1	2.3	1.6	6.9	3.6	14.4
	870	0	tr	tr	–	–	–	–	–	–	–	–	–
In_2O_3/H-ZSM-5[e]	30	100	0.2	4.8	28.8	27.1	14.3	12.2	2.6	1.4	4.7	3.9	12.6
	870	82.9	0.4	4.2	36.3	19.9	9.6	12.9	2.2	1.6	8.4	4.6	16.8

[a] Reaction conditions: 350 °C, WHSV = $1.3\,h^{-1}$, helium diluent $60\,ml\,min^{-1}$.

[b] Selectivities for C_2–C_{6+} hydrocarbons are quoted as alkene and alkane. tr = trace.

[c] H-ZSM-5 (0.125 g, Si : Al = 80) particles (0.6–1 mm) mixed with glass beads as diluent (0.125 g).

[d] Physical mixture of In_2O_3 with H-ZSM-S crushed 1 : 3 weight ratio (0.25 g, pellets, 0.6–1.0 mm).

[e] Physical mixture of In_2O_3 with H-ZSM-S crushed 1 : 9 weight ratio (0.25 g, pellets, 0.6–1.0 mm).

table 5, and it is apparent that enhanced C_8 and C_9 aromatic yields are observed with all three Si : Al ratios. A further set of experiments was then carried out with the Si : Al = 30 and 80 samples of H-ZSM-5 to determine the optimum amount of β-Ga_2O_3 for aromatic compound formation (table 6). In these experiments, H-ZSM-5 (Si : Al = 30) was used in two forms that had been subjected to different calcination conditions, either 350 °C for 3 h or 550 °C for 16 h. However, the calcination conditions of the zeolite prior to reaction were not found to be particularly significant, although the zeolite calcined at 550 °C was more stable and gave slightly higher aromatic yields. Interestingly, the Si : Al ratio of H-ZSM-5 did influence the optimum ratio of β-Ga_2O_3 required. With H-ZSM-5 (Si : Al = 80) the optimum ratio of β-Ga_2O_3/H-ZSM-5 is observed to be *ca.* 1 : 1. However, when more Al is present and, consequently, the concentration of Brønsted acid sites is higher, the optimum ratio of β-Ga_2O_3/H-ZSM-5 is found to be *ca.* 3 : 1. Hence, the effect is dependent upon the concentration of the acid sites present in the composite mixture. However, the highest yield of C_8 and C_9 aromatics is observed with H-ZSM-5 (Si : Al = 80) indicating that a lower concentration of acid sites with stronger Brønsted acidity might be preferred for the aromatization reaction.

3.3. *Effect of H_2 pretreatment and co-feeding on β-Ga_2O_3/H-ZSM-5 catalysts*

Recently, Raichle *et al.* [19] have reported that gallium-containing zeolite ZSM-5, prepared by the thermal method of Price and Kanazirev [20], could convert cycloalkanes to short-chain alkanes in a hydrogen

Table 5
Effect of Si : Al ratio on catalyst performance[a]

Catalyst[b]	Reaction time (min)	Methanol conversion (%)	Product selectivity (%)[c]										Aromatic hydrocarbon yield (%)
			CH_4	C_2	C_3	C_4	C_5	C_{6+}	C_6H_6	C_7H_8	C_8H_{10}	C_9H_{12}	
H-ZSM-5(30)[d]	30	100	0.3	8.4	36.7	20.5	12.5	10.0	4.0	0.8	3.3	3.3	11.5
	870	100	0.3	8.2	43.6	20.2	8.6	7.7	3.1	1.2	4.2	1.6	11.3
H-ZSM-5(30)/β-Ga_2O_3[e]	30	100	0.3	15.9	27.7	15.0	5.2	2.3	1.8	2.7	13.2	15.8	33.5
	870	87.4	1.1	16.6	31.9	14.4	7.9	4.7	2.5	2.0	9.9	9.8	26.4
H-ZSM-5(50)[d]	30	99.7	0.3	10.8	24.1	29.7	11.6	4.2	1.9	3.8	8.2	5.4	19.3
	870	99.8	0.5	11.1	29.9	31.7	11.6	5.6	1.9	1.7	6.5	3.4	13.5
H-ZSM-5(50)/β-Ga_2O_3[e]	30	100	0.5	15.8	22.6	15.8	5.8	2.2	1.6	3.6	17.6	15.0	37.3
	870	96.5	1.2	17.4	26.3	14.6	5.6	7.0	2.3	2.6	13.8	14.2	32.9
H-ZSM-5(80)[d]	30[e,f]	100	0.2	8.3	43.7	21.2	8.7	4.3	2.9	1.2	2.1	1.9	8.1
H-ZSM-5(80)/β-Ga_2O_3[e]	30	100	0.8	15.7	21.0	6.0	2.5	3.0	1.5	5.1	24.2	20.6	51.4
	870	100	0.9	13.2	30.6	9.3	4.1	3.5	1.3	3.3	18.4	18.5	38.5

[a] Reaction conditions: 400 °C, WHSV = $1.3\,h^{-1}$, helium diluent $60\,ml\,min^{-1}$.

[b] Figure in parentheses denotes Si : Al ratio.

[c] Selectivities for C_2–C_{6+} hydrocarbon are quoted as alkene and alkane. Alkene/alkane ratio typically 50 : 1.

[d] Zeolite (0.125 g) particles (0.6–1 mm) mixed with glass beads as diluent (0.125 g).

[e] H-ZSM-5 (0.125 g) and β-Ga_2O_3 (0.125 g) crushed together, pelleted, crushed and sieved to give particles (0.6–1 mm).

[f] Catalyst performance stable over 870 min test period.

Table 6
Effect of β-Ga_2O_3 loading on methanol conversion over β-Ga_2O_3/H-ZSM-5 catalysts[a]

Ga_2O_3 (wt%)	Methanol conversion (%)	Product selectivity (%)[b]										Aromatic hydrocarbon yield (%)
		CH_4	C_2	C_3	C_4	C_5	C_{6+}	C_6H_6	C_7H_8	C_8H_{10}	C_9H_{12}	
0	100[c]	0.4	11.1	27.7	27.3	9.0	3.1	1.2	3.7	9.6	9.8	24.3
	100[d]	0.3	8.4	36.7	20.5	12.5	10.0	4.0	0.8	3.3	3.3	11.5
	100[e]	0.2	8.3	43.7	21.2	8.3	4.3	2.9	1.2	2.1	1.9	8.1
10	100[c]	0.4	10.6	24.2	26.1	9.5	3.4	1.3	3.8	10.4	10.3	25.8
	100[d]	0.3	9.7	28.5	30.1	8.3	4.1	2.5	2.6	7.5	6.4	18.9
	100[e]	0.4	7.7	41.3	20.4	8.6	6.1	1.8	1.9	7.2	4.6	15.5
25	100[c]	0.4	16.3	24.5	17.0	5.9	2.4	1.1	3.6	14.2	14.7	33.6
	100[d]	0.3	12.5	30.0	21.6	8.1	3.5	2.5	2.1	9.7	9.7	24.1
	100[e]	0.6	11.7	32.5	10.7	4.1	3.2	1.9	3.4	14.2	17.8	37.2
50[f]	100[c]	0.3	14.9	23.6	17.3	4.8	1.4	0.8	6.1	16.3	15.2	38.5
	100[d]	0.3	15.9	27.7	15.0	5.2	2.3	1.8	2.7	13.2	15.8	33.5
	100[e]	0.5	15.7	21.0	6.0	2.5	3.0	1.5	5.1	24.2	20.6	51.4
50[g]	100[c]	0.7	12.1	23.6	24.6	8.5	3.0	1.2	3.7	11.8	10.7	27.5
	87.4[d]	1.1	16.6	31.9	14.4	7.9	4.7	2.5	2.0	9.9	9.8	26.4
	100[e]	0.9	13.2	30.6	9.3	4.1	3.5	1.3	3.3	15.4	18.5	38.5
75[f]	99.5[c]	0.6	18.5	20.5	10.0	3.5	4.8	1.0	2.9	15.0	23.4	42.3
	98.4[d]	0.6	20.2	23.4	8.3	3.4	2.8	0.8	3.9	17.0	19.5	42.3
	100[e]	0.4	9.8	28.5	11.5	4.6	8.6	2.4	3.7	17.8	20.6	39.6
75[g]	36.1[e]	2.5	17.2	26.7	8.8	5.7	6.2	0.9	3.0	12.3	16.6	32.8
	5.1[d]	15	26.7	25.0	12.2	10.5	9.7	–	–	–	–	0
	74.3[e]	1.8	15.3	30.5	10.7	5.6	5.2	1.6	2.3	12.3	14.7	30.8
90[f]	94.2[c]	0.9	22.4	20.6	8.8	4.1	3.0	1.4	3.0	16.0	19.7	40.1
	94.6[d]	0.7	18.5	26.3	11.1	4.1	5.9	2.7	2.7	13.7	13.2	33.9
	90.3[e]	0.7	17.0	24.8	9.9	5.0	9.1	3.4	2.4	10.7	16.1	32.3
90[g]	1.1[c]	70.7	12.5	16.8	–	–	–	–	–	–	–	0
	0.9[d]	58.9	26.7	14.4	–	–	–	–	–	–	–	0
	0.7[e]	54.9	27.7	17.5	–	–	–	–	–	–	–	0
100	0.5[c]	tr	tr	tr	tr	tr	–	–	–	–	–	0
	0.5[d]	tr	tr	tr	tr	tr	–	–	–	–	–	0
	0.5[e]	tr	tr	tr	tr	tr	–	–	–	–	–	0

[a] Reaction conditions: 400 °C, WHSV = $0.7\,h^{-1}$, He $60\,ml\,min^{-1}$.

[b] Selectivities for C_2–C^{6+} hydrocarbons quoted as total alkene and alkane; selectivities for 0, 10, 25 and 100 wt% Ga_2O_3 stable throughout reaction period of 870 min.

[c] H-ZSM-5 (Si : Al = 30) calcined 500 °C.

[d] H-ZSM-S (Si : Al = 30) calcined 350 °C.

[e] H-ZSM-5 (Si : Al = 80) calcined 550 °C.

[f] Initial time-on-line at 30 min.

[g] Final time-on-line at 870 min.

atmosphere. In this process, the catalyst requires a pretreatment in hydrogen prior to use. Gallium-containing zeolites are also essential for alkane aromatization [16–18]. However, this reaction requires temperatures in excess of 600 °C, *i.e.*, 300 °C higher than those used in the current study. Alkane aromatization over gallium-containing ZSM-5 has been found to be very sensitive to co-fed hydrogen [18]. This is not surprising since H_2 is a major product of the aromatization reaction and additional hydrogen tends to suppress alkane conversion [18]. In the alkane aromatization reaction the initial reaction is dehydrogenation to form the alkene, a reaction that requires a high temperature, which is oligomerized and aromatized, the latter step generating hydrogen. We therefore investigated the role of hydrogen pre-treatment and co-feeding in the aromatization reaction occurring with the β-Ga_2O_3/H-ZSM-5 composite catalyst used in this study. We have previously shown that hydrogen co-feeding does not affect the selectivity or activity of H-ZSM-5 as a catalyst for methanol conversion to hydrocarbons [21]. Hence, any observed effect can be ascribed to the aromatization process. Two sets of experiments were carried out and the results are shown in table 7. First, β-Ga_2O_3/H-ZSM-5 (Si:Al = 80) (1:1 by weight) was pretreated in H_2 at 500 °C for 6 h. Following the hydrogen treatment, methanol conversion was studied at 400 °C in the absence of co-fed hydrogen. The catalyst activity and the selectivity were not affected by extended reaction time for up to 870 min. However, the selectivity to C_8 and C_9 aromatics was significantly decreased compared with the same catalyst in the absence of the hydrogen pretreatment. In addition, the

Table 7
Methanol conversion with co-fed hydrogen or hydrogen pretreated catalysts[a,b]

H_2 treatment	Reaction time (min)	Methanol conversion (%)	Product selectivity (%)										Total aromatic selectivity (%)
			CH_4	C_2	C_3	C_4	C_5	C_{6+}	C_6H_6	C_7H_8	C_8H_{10}	C_9H_{12}	
H_2 pretreatment[c]	30	100	0.5	13.7	22.8	15.2	6.8	3.9	1.6	3.9	14.3	17.3	37.7
	870	100	0.8	13.7	26.9	13.6	5.9	2.2	2.5	3.1	15.2	16.1	36.9
H_2 cofed[d]	30	98.6	0.5	14.8	22.5	15.9	3.9	2.7	2.1	2.7	14.6	20.4	39.7
	150	98.5	0.6	15.9	25.9	8.8	3.6	5.9	2.2	4.3	14.9	17.9	39.3
	230[e]	93.6	0.4	12.1	19.4	6.1	3.0	6.7	2.1	3.4	17.2	29.5	52.2
	630[e]	67.3	1.4	15.0	28.1	9.2	4.6	10.3	1.0	2.5	12.1	15.2	30.8

[a] H-ZSM-5 (0.125 g Si : Al = 80) and β-Ga_2O_3 (0.125 g), crushed together, pelleted, crushed to give particles.
[b] Reaction conditions: 400 °C, WHSV = 1.3 h^{-1}, helium diluent 60 ml min^{-1}.
[c] Catalyst pretreated with H_2 (10% in Ar, 120 ml min^{-1}) 500 °C, 6 h.
[d] Reaction carried out with co-fed H_2, helium diluent replaced by H_2 (10% in Ar, 60 ml min^{-1}).
[e] H_2 replaced by helium (60 ml min^{-1}).

selectivity of C_4 hydrocarbon was enhanced and it appears that the hydrogen pretreatment affects the aromatization of C_4 alkenes. Second, β-Ga_2O_3/H-ZSM-5 (Si : Al = 80) (1 : 1 by weight) was investigated for methanol conversion in the presence of co-fed H_2. The conversion and selectivity are stable in the presence of co-fed H_2. However, although the methanol conversion is only slightly suppressed, the yield of aromatic hydrocarbon is significantly decreased and the C_4 selectivity was increased compared with the yield when H_2 was not co-fed (table 1). These effects are similar to those observed with the H_2-pretreated catalyst. When the H_2 co-feed is removed, the catalyst deactivates, which is not observed for the non-H_2-reacted catalyst (table 1). Interestingly, the aromatic selectivity increases to the same level as observed for the fresh catalyst in the absence of H_2 and the selectivity to C_2 and C_4 hydrocarbons was decreased (table 1). However, the selectivity to aromatics decreases with time on stream and the selectivity to C_3 and C_4 hydrocarbons increases. This is also observed for the non-H_2-treated catalyst (table 1) but, in this case, no deactivation is apparent.

3.4. *Methanol conversion over ZnO/H-ZSM-5 and MoO_3/H-ZSM-5 composite catalysts*

Previous studies have shown that ZnO/H-ZSM-5 and MoO_3/H-ZSM-5 composite catalysts are effective for the aromatization of alkanes [16,22,23]. In particular, ZnO/H-ZSM-5 catalysts have been found to be effective for propane aromatization whereas MoO_3/H-ZSM-5 catalysts are very active for methane aromatization. In view of this, these composite catalysts were examined for the methanol conversion reaction at 400 °C (table 8). Both composites were less active than H-ZSM-5 alone and, interestingly, there was no significant enhancement in the selectivity to aromatic hydrocarbons. Hence, the enhancement in aromatic yield is a feature of β-Ga_2O_3 and In_2O_3.

3.5. *Comments on the nature of the active site*

The addition of β-Ga_2O_3 to H-ZSM-5 as a simple mixture prepared using gentle agitation clearly leads to an enhancement in the yield of aromatic hydrocarbons,

Table 8
Methanol conversion over ZnO/H-ZSM-5 and MoO_3/H-ZSM-5[a]

Catalyst	Reaction time (min)	Methanol conversion (%)	Product selectivity (%)[b]										Aromatic hydrocarbon selectivity (%)
			CH_4	C_2	C_3	C_4	C_5	C_{6+}	C_6H_6	C_7H_8	C_8H_{10}	C_9H_{12}	
H-ZSM-5[c]	30[d]	100	0.1	3.8	39.1	27.5	6.6	11.5	4.5	1.3	3.9	1.7	11.4
ZnO/H-ZSM-5[e]	30[d]	97.0	0.2	4.8	42.0	19.8	11.9	7.7	3.8	1.8	5.2	2.9	13.6
MoO_3/H-ZMS-5	30	86.0	4.4	5.8	34.6	18.9	11.2	10.8	4.0	1.6	4.9	3.9	14.3
	870	83.5	0.4	4.5	40.3	21.8	12.5	10.2	4.5	1.2	2.9	1.8	10.3

[a] Reaction conditions: 400 °C, WHSV = 1.3 h^{-1}, helium diluent 60 ml min^{-1}.
[b] Selectivity to C_2–C_{6+} hydrocarbon quoted as alkene and alkane.
[c] Catalyst performance stable for 870 min.
[d] H-ZSM-5 (Si : Al = 80, 0.125 Sg) pellets (0.6–1.0 mm) diluted with glass beads (0.125 g).
[e] H-ZSM-5 (Si : Al = 80, 0.125 g) and the oxide (0.125 g) crushed together, pelleted, sieved to give particles (0.6–1.0 mm).

particularly xylenes, ethylbenzene and trimethylbenzene, at the expense of C_3–C_6 alkenes. A number of previous studies have considered gallium modification of zeolites for the methanol conversion reaction [24] but none of these earlier studies have indicated an enhancement in the formation of aromatic hydrocarbons. Kijueua *et al.* [25] studied the isomorphous substitution of Ga, Fe and B for Al in erionite and mordenite for the conversion of methanol to alkenes. Although no specific effects for Ga substitution were noted, dealumination was found to improve the catalyst lifetime. Sawa *et al.* [5,24,26] showed that Ga^{3+} exchange of mordenite decreased the aromatic hydrocarbon selectivity. Inui *et al.* [27] studied isomorphously-substituted ZSM-5 catalysts and Ga-substituted ZSM-5 was the least selective for light alkenes in the methanol conversion reaction. Al-Jarallah *et al.* [28] studied methanol conversion over a highly silaceous pentasil zeolite at 400 °C that had been impregnated with a series of metal nitrates (Ag, Ca, Cd, Cu, Ga, In, La and Sr). Incorporation of gallium nitrate was not found to increase the yield of aromatic hydrocarbons in their study; however, it is possible that the nitrate may have only partially decomposed with their reaction conditions.

The present study indicates that composite catalysts, in which an oxide is mixed with a zeolite, may provide a relatively simple approach to enable control of the product distribution for the methanol conversion reaction, and clearly this general approach requires further detailed investigation. In the present study, enhancement in the rate of hydrocarbon formation from methanol conversion is observed with β-Ga_2O_3/H-ZSM-5 and In_2O_3/H-ZSM-5 composite catalysts. It is interesting to note that In-doped H-ZSM-5, in which the In is introduced into the H-ZSM-5 by a solid-state reaction [29,30], has been shown to be much less active for the conversion of methanol to hydrocarbon than the parent H-ZSM-5 zeolite. In the present study, the effects observed with the addition of In_2O_3 are found to be sensitive to the method of preparation, and the most stable catalysts are formed when the In_2O_3 and H-ZSM-5 are not intimately mixed.

As noted above, we consider that the active site is formed in these composite catalysts at the junction between the crystallites of the oxide and H-ZSM-5. This is a form of contact synergy, a phenomenon that is well documented for other oxides [31,32]. At this site, it is considered that light alkenes, formed in the methanol conversion reaction over H-ZSM-5, can be aromatized to form C_8 and C_9 aromatic molecules. However, the data for the catalytic reactions carried out at 300 °C indicate that these sites can also play a role in the initial activation of methanol. This is an important result. It is possible that the site involves the interplay of a Brønsted acid site on the surface of the zeolite crystallite with hydroxyl groups on the surface of the oxide. The experiments carried out with H-ZSM-5 with different Si : Al ratios confirms this and indicates that fewer stronger acid sites may be preferable to observe the highest enhancement in aromatic yield. In addition, the oxidation state of the oxide cation at the junction site could play an important part in the activation of methanol. Detailed spectroscopic experiments are now planned to investigate the nature of the active site in these composite catalysts. However, the experiments carried out in the presence of hydrogen show that the aromatic formation is decreased for the β-Ga_2O_3/H-ZSM-5 composite catalyst. This is analogous to the effects observed in propane aromatization over similar catalysts [16,18] and this may indicate that the active site is similar to that responsible for propane aromatization in these catalysts.

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