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Conversion of Methanol to Hydrocarbons over Ga_2O_3/H-ZSM-5 and Ga_2O_3/WO_3 Catalysts

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The conversion of methanol over physical mixtures of Ga_2O_3 and H-ZSM-5 or WO_3/γ-Al_2O_3 is reported. The addition of Ga_2O_3 to H-ZSM-5 markedly increases the selectivity to aromatic hydrocarbon at the expense of C_2–C_4 alkenes, without affecting the overall conversion. This effect is obtained at temperatures $\geq 400^\circ C$, and the maximum effect is observed at 1 : 1 mixtures of Ga_2O_3 and H-ZSM-5. Experiments using separate beds of Ga_2O_3 and H-ZSM-5 with different configurations do not reveal any significant effect. In addition, upon removal of Ga_2O_3 from the Ga_2O_3/H-ZSM-5 physical mixture the normal catalytic performance of the zeolite is observed. Ga_2O_3 is also shown to significantly enhance the catalytic activity of a WO_3/γ-Al_2O_3 catalyst when it is incorporated as a physical mixture. The results are explained in terms of a new active site that is formed at the point of contact between Ga_2O_3 and H-ZSM-5 or WO_3/γ-Al_2O_3 particles. In the case of H-ZSM-5/β-Ga_2O_3, this site catalyzes the formation of aromatic products from C_2–C_5 alkenes, whereas for $WO_3/\gamma Al_2O_3$:β-Ga_2O_3 the new site catalyzes the formation of methane. © 2002 Elsevier Science

Key Words: **methanol conversion to hydrocarbons; contact synergy; Ga_2O_3/H-ZSM-5 catalyst; Ga_2O_3/WO_3 catalyst.**

INTRODUCTION

Methanol conversion to hydrocarbons has been well studied (1–20), since Chang and Silvestri reported this reaction using H-ZSM-5 as catalyst (21). Subsequently, it was shown that WO_3 supported on γ-Al_2O_3 could also catalyze this reaction (22); however, the hydrocarbon yield was far superior with zeolite catalysts. The extensive literature concerning the conversion of methanol to hydrocarbons over zeolite catalysts has recently been reviewed by Vora *et al.* (33) for the formation of light alkenes, and earlier reviews have discussed the conversion of methanol to gasoline (24–26). The reaction has been observed with a range of zeolites and microporous materials, e.g., zeolite Y (27); zeolite β (28); mordenite (29); $AlPO_4$-5, SAPO-5, and MeAPO-5 (30); zeolite EU-2 (31); clinoptitolite (32); and SAPO-34 (33); as well as nonzeolite catalysts, e.g., 12-tungstophosphoric acid (34).

Most of the attention has been focused on the reaction mechanism for the formation of the initial carbon–carbon bond (26). Two types of mechanisms, i.e., the consecutive- and parallel-type mechanisms, have received extensive experimental support (35). For the consecutive-type mechanism a pathway has been proposed (9, 10, 36–38) involving surface methylation and deprotanation to either a surface-adsorbed carbene or a methylene oxonium ylide, which is isoelectronic with a gas-phase carbene. The surface-adsorbed intermediate reacts with either methanol or dimethyl ether to form the initial carbon–carbon bond. For the parallel-type mechanism, Dahl and Kolboe (35, 39) have proposed that a hydrocarbon pool, with characteristics similar to coke, participates in a carbon–carbon bond formation. Most recently, extensive theoretical studies have been carried out on this reaction using density functional theory (40–44). In particular, Sinclair and Catlow (44) showed that the calculated activation energy for the surface bond methylene carbene is similar to that observed experimentally for the methanol conversion reaction, providing support for this pathway. However, most recently, Tajima *et al.* (42) used theoretical calculations to indicate that CO and CH_4/CH_2O are also potential reactions intermediates, although no experimental evidence currently supports this proposal.

Most surprisingly, there has been remarkably little attention given to the use of composite zeolite catalysts, in which a zeolite is mixed with a second component. The addition of Fe_2O_3 to a zeolite catalyst was described by Qinghua *et al.* (45), and was shown to affect both conversion and selectivity. The lack of attention to a composite catalyst is even more surprising given the extensive literature concerning Ga_2O_3/H-ZSM-5 catalysts for the aromatization of propane (46–48). In this reaction physical mixtures of Ga_2O_3 and H-ZSM-5 are found to have a significantly different catalytic behavior from that of the pure materials. We have now found that the addition of Ga_2O_3 to H-ZSM-5 can significantly affect the product distribution for the methanol-to-hydrocarbon reaction, and in this paper we report the findings.

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EXPERIMENTAL

Zeolite H-ZSM-5 (Si/Al ratio = 80) and gallium oxide (β-Ga_2O_3) were obtained as commercial samples from PQ Corporation and Aldrich, respectively. γ-WO_3/γAl_2O_3 was prepared as previously described (10). Gallium oxide and either H-ZSM-5 or WO_3/γAl_2O_3 were physically mixed with and without crushing. Catalytic reactions were carried out using a stainless-steel microreactor. Methanol was fed to the reactor using a calibrated syringe pump and mixed with a helium diluent prior to vaporization. The helium flow rate was controlled using a mass flow controller. Catalyst samples (typically 0.2–0.3 g) were contained in the heated zone of a tubular microreactor (9-mm i.d), and all lines to and from the reactor were heated to avoid the condensation of products. Product analysis was carried out by on-line gas chromatography using a Poropac Q column (2m × 3 mm). Catalysts were characterized using powder X-ray diffraction.

RESULTS

Methanol Conversion with H-ZSM-5, Ga_2O_3, and Ga_2O_3/H-ZSM-5

Methanol conversion was investigated over H-ZSM-5, β-Ga_2O_3, and β-Ga_2O_3/H-ZSM-5. In all cases the total mass of material in the reactor was maintained at 0.25 g using glass beads as an inert diluent. The results for the reactions at 400°C are shown in Table 1. Methanol conversion over H-ZSM-5 gives very similar results under these reaction conditions when compared to previous studies (9, 10). The replacement of the glass beads with boron nitride powder, a material that is inert for methanol conversion, is not found to have any significant effect in the catalytic performance. β-Ga_2O_3 oxide is found to be almost inert for methanol conversion under these reaction conditions; only traces of C_1–C_5 hydrocarbons were observed, and these were mainly alkenes. The conversion of methanol over a physical mixture of β-Ga_2O_3 and H-ZSM-5, in either powder or pellet form, gave surprising results, since the aromatic product yield was significantly increased, and the yield of C_3 and C_4 alkenes was decreased. In this experiment the two powders were mixed together by gentle agitation in a glass tube in the absence of grinding. The catalytic activity of the physical mixture was stable during the period of the experiment, ca. 1000 min. It is apparent that the effect of enhanced aromatic formation is only observed at very high conversion (>99%) and at high temperatures. It has, therefore, not proved possible, to date, to investigate the effect of enhanced aromatic compound formation at lower conversions. In a subsequent experiment the physical mixture of β-Ga_2O_3/H-ZSM-5 was ground to give a more intimate mixture. Methanol conversion over this material gave, initially, an extremely high aromatic product yield, >50 wt% (Table 1). However, in this case the catalytic activity was not stable (Table 1), the catalytic performance gradually declined, and the yield of aromatic product was slightly decreased.

Effect of Ga_2O_3 Loading in Ga_2O_3/H-ZSM-5 Catalysts

A series of experiments were carried out using physical mixtures of β-Ga_2O_3/H-ZSM-5, which were prepared by grinding the two powders together to ensure an intimate mixture. The results (Table 2) show that the highest yields of aromatic hydrocarbons are obtained for the 1 : 1 physical mixture. Catalysts containing up to 25 wt% Ga_2O_3 are

TABLE 1

Methanol Conversion over H-ZSM-5 and β-Ga_2O_3/H-ZSM-5 Catalysts[a]

Catalyst	Methanol conversion (%)	Product selectivity (wt%)[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]	100	0.2	8.8	38.4	27.6	10.4	5.5	2.4	1.4	3.4	2.7	10.4
H-ZSM-5/BN[d]	100	0.2	6.3	36.1	28.2	12.6	7.3	3.1	1.1	2.7	5.5	9.3
β-Ga_2O_3/glass beads[e]	0.5	tr	tr	tr	tr	tr	—	—	—	—	—	0
H-ZSM-5/β-Ga_2O_3 mixed[f]	100	0.3	6.5	35.5	21.9	12.7	4.9	4.6	2.2	5.9	5.5	18.2
H-ZSM-5/β-Ga_2O_3 crushed[g]	100	0.8	15.7	21.0	6.0	2.5	3.0	1.5	5.1	24.2	20.6	51.4
H-ZSM-5/β-Ga_2O_3 crushed[h]	100	0.9	13.2	30.6	9.3	4.1	3.5	1.3	3.3	15.4	18.5	38.5

[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 alkene and alkane, typically alkene/alkane >50 mol ratio.

[c] H-ZSM-5 (0.125 g, pellets, 0.6–1.0 mm) mixed with glass beads (0.125 g).

[d] H-ZSM-5 (0.125 g, pellets, 0.6–1.0 mm) mixed with boron nitride (0.125 g, pellets, 0.25–0.3 mm).

[e] β-Ga_2O_3 (0.125 g, pellets, 0.25–0.3 mm) mixed with glass beads (0.125 g).

[f] Physical mixture of β-Ga_2O_3 (0.125 g, pellets, 0.25–3.0 mm) with H-ZSM-5 (0.125 g, pellets, 0.6–1.0 mm); not crushed.

[g] As *f*, crushed, 30 min time on line (0.25 g, pellets, 0.6–1 mm).

[h] As *g*, 870 min time on line.

TABLE 2

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 (wt%)[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	0.2	8.3	43.7	21.2	8.3	4.3	2.9	1.2	2.1	1.9	8.1
10	100	0.4	7.7	41.3	20.4	8.6	6.1	1.8	1.9	7.2	4.6	15.5
25	100	0.6	11.7	32.5	10.7	4.1	3.2	1.9	3.4	14.2	17.8	37.2
50[c]	100	0.5	15.7	21.0	6.0	2.5	3.0	1.5	5.1	24.2	20.6	51.4
50[d]	100	0.9	13.2	30.6	9.3	4.1	3.5	1.3	3.3	15.4	18.5	38.5
75[c]	100	0.4	9.8	28.5	11.5	4.6	8.6	2.4	3.7	17.8	20.6	39.6
75[d]	74.3	1.8	15.3	30.5	10.7	5.6	5.2	1.6	2.3	12.3	14.7	30.8
90[c]	90.3	0.7	17.0	24.8	9.9	5.0	9.1	3.4	2.4	10.7	16.1	32.3
90[d]	0.7	54.9	27.7	17.5	—	—	—	—	—	—	—	0
100	0.5	tr	tr	tr	tr	tr	—	—	—	—	—	0

[a] Reaction conditions: 400°C, WHSV $= 0.7\ h^{-1}$, He 60 ml min^{-1}, catalyst = 0.25 g.

[b] Selectivities for C_2–C_{6+} hydrocarbons quoted as total alkene and alkane.

[c] Initial time on line at 30 min.

[d] Final time on line at 870 min.

stable over the test period, ca. 900 min. However, catalysts containing higher levels of β-Ga_2O_3 gradually deactivate, and the yield of aromatic products declines. It is clear that even with 10 wt% β-Ga_2O_3 a significant enhancement in the yield of aromatic products is observed. The enhancement is particularly apparent for xylenes and trimethylbenzenes, and there is very little effect observed for the yields of benzene and toluene. In general the yield of C_3–C_5 alkenes declines, as the yield of C_8 and C_9 aromatic product is enhanced.

Effect of Reaction Conditions on Methanol Conversion over Ga_2O_3/H-ZSM-5

The effect of temperature and methanol weight-hourly space velocity (WHSV) on methanol conversion over H-ZSM-5 and β-Ga_2O_3/H-ZSM-5 physical mixtures are shown in Fig. 1 and Tables 3 and 4. In these experiments a 1 : 1 physical mixture of β-Ga_2O_3 and H-ZSM-5, prepared by gentle agitation of the pellets in a glass tube without grinding, was used. Below 400°C, the addition of β-Ga_2O_3 had no effect on the product distribution of H-ZSM-5. At 400°C, the enhancement in aromatic yield becomes apparent (Table 3); however, the β-Ga_2O_3/H-ZSM-5 catalyst is not stable, the catalyst activity declines (Fig. 1b), and the yield of aromatic compounds also decreases. In a subsequent set of experiments, the methanol WHSV was varied at a constant temperature of 400°C. It is apparent that for all methanol flow rates the enhancement in the yield of aromatic products is observed, and in general the yields of C_3 and C_{4+} alkenes are decreased (Table 4).

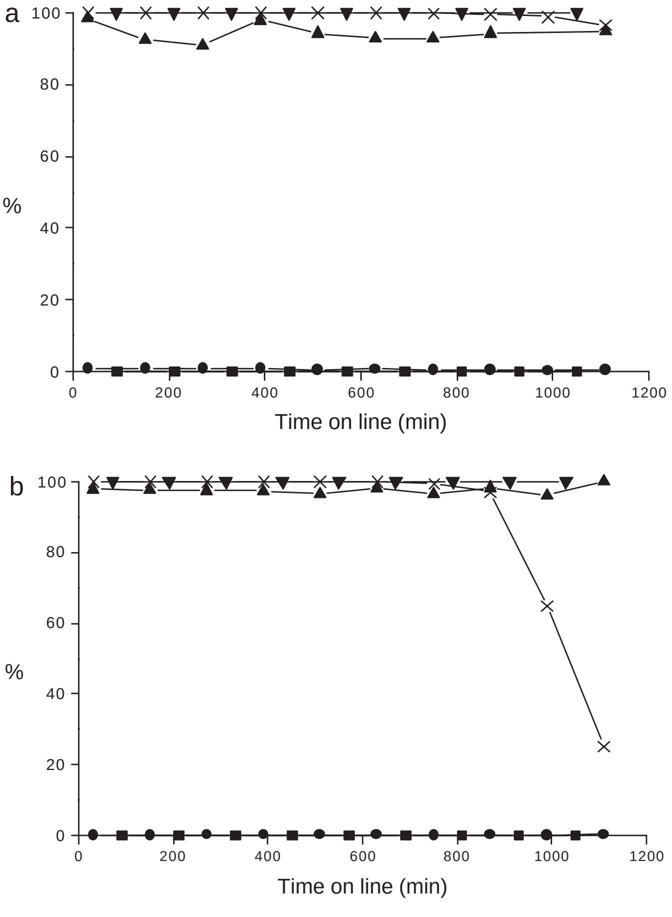

FIG. 1. Methanol conversion to hydrocarbons as a function of temperature: (a) methanol conversion over H-ZSM-5/glass beads; (b) methanol conversion over β-Ga_2O_3/H-ZSM-5 1:1 physical mixture; Key: ■, 200°C; ●, 300°C; ▲, 350°C; ▼, 400°C; X, 500°C; WHSV $= 0.56\ h^{-1}$.

TABLE 3

Effect of Temperature on Product Selectivity[a]

Temperature (°C)	H-ZSM-5 (wt%)[b]										β-Ga_2O_3/H-ZSM-5 (wt%)[c]									
	Conv.	CH_4	C_2	C_3	C_{4+}	C_6H_6	C_7H_8	C_8H_{10}	C_9H_{12}	Ar_{tot}[d]	Conv.	CH_4	C_2	C_3	C_{4+}	C_6H_6	C_7H_8	C_8H_{10}	C_9H_{12}	Ar_{tot}[d]
200	tr	tr	—	—	tr	—	—	—			0	—	—	—	—	—	—	—	—	0
300	0.6	0.6	23.2	31.5	44.7	0	0	tr	0	tr	0.1	3.2	48.0	48.7	tr	—	—	—	—	0
350	94.3	0.2	11.6	18.5	53.9	1.8	1.0	5.7	7.3	15.8	97.5	0.2	11.8	17.6	54.5	1.7	1.0	5.8	7.4	15.9
400	100	0.2	10.4	40.7	39.0	3.2	1.2	2.9	2.4	9.7	100	0.6	10.9	40.6	32.1	2.8	2.2	5.5	5.3	15.8
500	100	0.5	19.3	46.4	26.3	1.9	1.3	2.9	1.4	7.5	100	0.7	18.5	41.1	22.0	0.8	3.6	8.4	4.9	17.7

[a] Reaction conditions: WHSV = 3.1 h^{-1}, He 60 ml min^{-1}.
[b] H-ZSM-5 (0.125 g, pellets, 0.6–1.0 mm) physically mixed with glass beads (0.125 g).
[c] H-ZSM-5 (0.125 g, pellets, 0.6–1.0 mm) physically mixed with β-Ga_2O_3 (0.125 g, pellets, 0.25–0.3 mm).
[d] Total aromatic products.

Methanol Conversion over Separate and Mixed Beds of Ga_2O_3 and H-ZSM-5

A series of experiments were carried out using separate beds of β-Ga_2O_3 and H-ZSM-5 separated by glass beads. Three different configurations were investigated:

1. H-ZSM-5 (0.125 g, pellets) and β-Ga_2O_3 (0.125 g, pellets), physically mixed using gentle agitation;
2. H-ZSM-5 (0.125 g, pellets) over β-Ga_2O_3 (0.125 g, pellets), the two beds separated by glass beads (1.0 g);
3. β-Ga_2O_3 (0.125 g, pellets) over H-ZSM-5 (0.125 g, pellets), the two beds separated by glass beads (1.0 g).

The conversion of methanol was investigated at 400°C for 1200 min time on line, and as expected the physical mixture of β-Ga_2O_3 and H-ZSM-5 (configuration 1) gave a sustained enhancement in the yield of aromatic compounds, as noted previously (Tables 1, 3, and 4). However, this was not observed when separate beds of β-Ga_2O_3 and H-ZSM-5 were reacted (i.e., configurations 2 and 3), and, in this case, there was no significant effect of the β-Ga_2O_3 component on the overall catalyst performance. These results indicate that it is the contact between the β-Ga_2O_3 and the H-ZSM-5 zeolite that is required to observe the enhancement in aromatic yield, since the yield enhancement is not observed when the materials are not in contact. In particular, the experiments with configuration 2 show that the effect is not caused by the products formed by H-ZSM-5 being sequentially reacted on the β-Ga_2O_3 to form aromatic compounds.

A further set of experiments was conducted using a catalyst prepared by mixing 50% β-Ga_2O_3 pellets (0.25–0.3 mm) with 50% H-ZSM-5 pellets (0.6–1.0 mm), prepared by pelleting and sieving the zeolite. The two materials were mixed using gentle agitation in a glass tube in the absence of grinding. The results for methanol conversion at 400°C over the physical mixture are shown in Fig. 2a. It is apparent that the enhancement in the yield of aromatic products is observed, and the yield of C_6–C_9 aromatic products is typically >20 wt%. After a 270-min reaction the flow of methanol was stopped, and the catalyst was cooled in flowing helium to room temperature. Once cooled, the catalyst was removed from the reaction

TABLE 4

Effect of Methanol WHSV on Product Selectivity[a]

Methanol WHSV (h^{-1})	H-ZSM-5 (wt%)[b]										β-Ga_2O_3/H-ZSM-5 (wt%)[c]									
	Conv.	CH_4	C_2	C_3	C_{4+}	C_6H_6	C_7H_8	C_8H_{10}	C_9H_{12}	Ar_{tot}[d]	Conv.	CH_4	C_2	C_3	C_{4+}	C_6H_6	C_7H_8	C_8H_{10}	C_9H_{12}	A_{tot}[d]
0.48	100	0.1	6.0	52.1	36.9	3.2	0.6	0.9	0.2	4.9	100	0.3	6.0	45.8	28.9	3.3	3.0	7.2	5.5	19.0
0.7	100	0.2	6.1	54.3	34.6	3.8	0.3	0.7	tr	4.8	100	0.2	5.9	41.2	37.7	3.0	2.1	4.8	4.3	15.0
1.3	100	0.1	6.3	38.2	47.3	3.1	1.4	2.7	2.0	9.2	100	0.2	5.9	44.5	31.1	2.1	3.7	5.9	5.3	18.3
3.1	100	0.2	10.4	40.7	39.0	3.2	1.2	2.9	2.4	9.7	100	0.6	10.9	40.6	32.1	3.7	2.2	5.5	5.3	15.8
4.6	93.0	0.2	4.8	41.2	47.8	2.6	0.6	1.6	1.2	6.0	99.9	0.2	8.2	37.6	43.3	1.2	1.2	3.5	3.3	10.7

[a] Reaction conditions: 400°C, He 60 ml min^{-1}.
[b] H-ZSM-5 (0.125 g, pellets, 0.6–1.0 mm) physically mixed with glass beads (0.125 g).
[c] H-ZSM-5 (0.125 g, pellets, 0.6–1.0 mm) physically mixed with β-Ga_2O_3 (0.125 g, pellets, 0.25–1.0 mm).
[d] Total aromatic products.

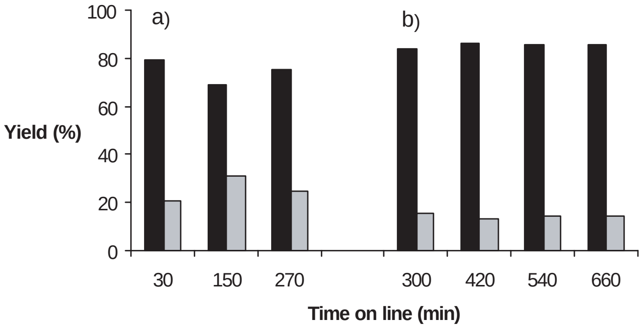

FIG. 2. Methanol conversion to hydrocarbons over (a) β-Ga_2O_3 (powder)/H-ZSM-5 (pellets) physical mixture until 270 min time on line, and (b) H-ZSM-5 (pellets) following removal of β-Ga_2O_3 (powder) by sieving after 270 min time on line. Reaction conditions: 400°C, WHSV 0.57 h^{-1}. Key: dark, nonaromatic hydrocarbons; light grey, aromatic hydrocarbons. All data recorded at 100% methanol conversion.

carefully and sieved to separate the β-Ga_2O_3 from the zeolite. Analysis of the two components using powder X-ray diffraction indicated that no changes occurred during the reaction to the crystallinity of these materials. In addition, analysis of the zeolite using atomic absorption spectroscopy confirmed that no significant level of β-Ga_2O_3 was retained with the zeolite pellets after the careful sieving procedure. Both materials were then investigated for methanol conversion using the same methanol flow rate as that used for the physical mixture. The β-Ga_2O_3 was found to be inactive. However, the zeolite still gave 100% methanol conversion (Fig. 2b), but the yield of aromatic hydrocarbon was now much lower, typically 13–14 wt% under these reaction conditions. This experiment demonstrates that the new catalytic active site formed by physically mixing β-Ga_2O_3 and H-ZSM-5 can be readily removed by separating the mixture.

Reaction of o-Xylene and Heptane over H-ZSM-5 and Ga_2O_3/H-ZSM-5

o-Xylene was reacted over H-ZSM-5 and β-Ga_2O_3/H-ZSM-5 catalysts at 600°C, and the results are given in Table 5. This temperature was used, as very little reaction was observed at lower temperatures. As expected, the H-ZSM-5 gives mainly *p*-xylene with some disproportionation to toluene, benzene, and trimethylbenzene. The addition of β-Ga_2O_3, without grinding does not significantly affect the catalytic performance, but does give a slight increase in the selectivity to toluene. The two catalysts show only a small decrease in catalyst activity over the time scale of the experiment. In contrast, the physical mixture of β-Ga_2O_3/H-ZSM-5 prepared by grinding shows a rapid decline in catalyst activity, although initially it has a similar catalytic performance to the other two catalysts.

In a similar experiment heptane (WHSV = 0.7 h^{-1}) was reacted over H-ZSM-5 and a β-Ga_2O_3/H-ZSM-5 physical mixture and prepared by gentle agitation at 400°C. Both catalysts gave total heptane conversion over the time scale of the experiment (1110 min). The product distribution for the two catalysts was very similar with virtually all the heptane being dehydrogenated to heptene (ca. 92–93%) and traces of lighter alkenes and alkanes being formed by cracking. No C_{8+} aromatic products were observed.

Methanol Conversion over WO_3-γ-Al_2O_3 and Ga_2O_3/WO_3-γ-Al_2O_3 Catalysts

As noted earlier, a 10 wt% WO_3-supported γ-Al_2O_3 catalyst has been found to be effective for the conversion of methanol to hydrocarbons (10, 22). A series of experiments were therefore carried out to determine if the addition of β-Ga_2O_3 to a 10 wt% WO_3-supported γ-Al_2O_3 catalyst would have a similar effect on the catalytic performance of the catalyst for methanol conversion. The results are shown in Table 6. At 450°C, the WO_3-γAl_2O_3 catalyst gives mainly CH_4, C_2H_4, and C_2H_6, as previously noted (10). Interestingly, the addition of β-Ga_2O_3 as a physical mixture increases the methanol conversion markedly; however, the increased yield is solely to methane. In this case no C_{2+} products, and in particular no aromatic products, are observed initially. Although the catalyst activity declines

TABLE 5

Reaction of *o*-Xylene over H-ZSM-5 and β-Ga_2O_3/H-ZSM-5[a]

	H-ZSM-5 (wt%)[b]					β-Ga_2O_3/H-ZSM-5 (wt%)[c]					β-Ga_2O_3/H-ZSM-5 (wt%) crushed[d]				
Time (min)	Conv.	C_6H_6	C_7H_8	C_8H_{10}[e]	C_9H_{12}	Conv.	C_6H_6	C_7H_8	C_8H_{10}[e]	C_9H_{12}	Conv.	C_6H_6	C_7H_8	C_8H_{10}[e]	C_9H_{12}
30	79.1	1.0	12.6	81.5	4.9	79.4	1.5	16.6	77.0	4.9	73.2	2.2	16.9	79.5	1.4
390	78.3	0.7	10.7	83.8	4.8	78.1	1.2	14.5	80.0	4.7	57.7	1.0	9.0	89.3	0.7
870	77.8	0.6	9.9	84.9	4.6	77.1	1.0	13.2	81.3	4.5	41.9	1.0	8.3	90.2	0.5
1350	78.3	1.1	13.6	82.6	2.7	76.4	1.0	12.7	82.1	4.2	27.7	1.0	8.6	90.2	0.2

[a] Reaction conditions, *o*-xylene WHSV = 0.7 h^{-1}, He 60 ml min^{-1}, catalyst 0.25 g, 400°C.

[b] H-ZSM-5 (0.125 g, pellets, 0.6–1.0 mm) mixed with glass beads (0.125 g).

[c] β-Ga_2O_3 (0.125 g, pellets, 0.6–1.0 mm) physically mixed with H-ZSM-5 (0.125 g, pellets, 0.6–1.0 mm) by gentle agitation.

[d] As in *c*, but the powders ground to give an intimate mixture.

[e] 95% *p*-xylene.

TABLE 6

Conversion of Methanol over 10% WO_3–γ-Al_2O_3 and β-Ga_2O_3/10% WO_3-γ-Al_2O_3[a]

Time (min)	Conversion (%)	Product selectivity (wt%)									
		CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_{4+}	C_6H_6	C_7H_8	C_8H_{10}	C_9H_{12}
30[b]	24.9	75.5	5.7	3.8	3.9	0.4	3.2	0.4	0.8	0.2	6.1
150[b]	16.6	84.0	4.2	4.5	3.0	0.5	2.8	0.3	0.7	0.1	0.0
270[b]	11.3	86.3	3.8	4.6	2.7	0.5	1.9	0.2	0.0	0.0	0.0
390[b]	8.8	86.6	3.6	4.5	2.4	0.5	2.3	0.2	0.0	0.0	0.0
510[b]	7.1	87.5	3.5	4.4	2.2	0.5	1.9	0.0	0.0	0.0	0.0
630[b]	4.8	87.7	3.3	4.2	1.9	0.5	2.4	0.0	0.0	0.0	0.0
750[b]	3.7	90.2	3.3	4.2	1.8	0.5	0.0	0.0	0.0	0.0	0.0
870[b]	3.5	90.4	3.2	4.2	1.8	0.5	0.0	0.0	0.0	0.0	0.0
30[c]	98.4	72.6	6.6	3.7	4.4	0.5	5.1	0.4	1.0	1.4	4.3
150[c]	27.5	81.9	3.9	3.7	2.8	0.4	5.4	0.6	1.3	0.0	0.0
270[c]	40.1	80.1	3.6	3.5	2.2	0.4	1.7	0.4	8.1	0.0	0.0
390[c]	9.6	88.2	3.4	3.8	2.0	0.4	1.9	0.3	0.0	0.0	0.0
510[c]	6.9	89.3	3.3	3.7	1.9	0.4	1.3	0.0	0.0	0.0	0.0
630[c]	5.8	90.1	3.2	3.6	2.2	0.0	0.8	0.0	0.0	0.0	0.0
750[c]	5.9	90.5	3.2	3.6	1.5	0.3	0.9	0.0	0.0	0.0	0.0
870[c]	3.5	90.4	3.2	4.2	1.8	0.5	0.0	0.0	0.0	0.0	0.0

[a] Reaction conditions: methanol WHSV = 0.65 h^{-1}, He 60 ml min^{-1}, 450°C.

[b] 10 wt% WO_3 supported on γ-Al_2O_3 (0.25 g, pellets, 0.6–1.0 mm) mixed with glass beads (0.25 g).

[c] 10 wt% WO_3 supported in γ-Al_2O_3 (0.25 g, pellets, 0.6–1.0 mm) mixed with β-Ga_2O_3 (0.25 g, pellets, 0.25–0.3 mm).

during the experiment, the conversion is still significantly higher than that observed with WO_3-γAl_2O_3 alone.

DISCUSSION

Contact Synergy between β-Ga_2O_3 and H-ZSM-5

The addition of β-Ga_2O_3 to H-ZSM-5 as a simple physical mixture prepared using gentle agitation clearly leads to an enhancement in the yield of aromatic hydrocarbons, particularly xylenes, ethylbenzene, and trimethybenzene, at the expense of C_3–C_5 alkenes. It is concluded that the active sites for the formation of aromatics are formed by the contact between crystallites of β-Ga_2O_3 and H-ZSM-5, which represents a clear example of contact synergy for this composite catalyst. Two additional experimental data support this conclusion. First, when a crushed mixture is used, the effect is enhanced markedly; this is consistent with the increased contact between β-Ga_2O_3 and H-ZSM-5 that would be created due to grinding the two powders together. Second, by using pellets of H-ZSM-5 and β-Ga_2O_3 as a powder, we demonstrated that the active site for aromatic formation can be first constructed and then removed by separating the two materials.

When β-Ga_2O_3 and H-ZSM-5 are mixed without crushing, the effect can be observed for a long period of time, and no deactivation is apparent. However, when the crushed physical mixture is used, although the catalyst activity for aromatic synthesis is markedly enhanced, the catalyst rapidly deactivates. During deactivation two effects are apparent: first, the selectivity to methane is enhanced, and second, the selectivity to aromatic hydrocarbons is decreased. The enhancement in methane selectivity during the deactivation of zeolite catalysts in the methanol conversion reaction has been commented on previously (9, 10), and is considered to be due to enhanced hydride donation to a surface methoxyl intermediate. The loss of activity is considered to be associated with coke formation deactivating the contact synergy active sites.

A number of previous studies have considered gallium modification of zeolites for the methanol conversion reaction (29, 49–53), but none of these earlier studies have indicated an enhancement in the formation of aromatic hydrocarbons. Kljueva *et al.* (49) studied the isomorphous substitution of Ga, Fe, and β for Al in erionite and mordenite for the methanol-to-olefin reactions. No specific effects for Ga substitution were noted, but dealumination was found to improve the catalyst lifetime. Sawa *et al.* (29, 50, 51) showed that Ga^{3+} exchange of mordenite decreased the aromatic hydrocarbon selectivity. Inui *et al.* (52) studied isomorphously substituted ZSM-5 catalysts, and found that Ga-substituted ZSM-5 was the least selective for light alkenes in the methanol conversion reaction. Al-Jarallah *et al.* (53) 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 to the oxide in this study.

In our study, the observation of a sustained catalytic effect on adding β-Ga_2O_3 to H-ZSM-5 (Si/Al = 80) is therefore surprising and unexpected.

We have previously shown that β-Ga_2O_3 has the highest rate for the hydrogen–deuterium exchange reaction over simple oxides (54). This finding indicated that β-Ga_2O_3 can readily activate C–H bonds, and we showed that when β-Ga_2O_3 was mixed with MoO_3 as a physical mixture, using gentle agitation, improved selectivity for methanol formation from the partial oxidation of methane was observed (54). In this case neither the β-Ga_2O_3 nor the MoO_3 showed any significant selectivity for methanol, and it was only the combination of the two oxides that created the new active site. Prior to this work, Ga-doped H-ZSM-5 has been extensively studied for the propane aromatization reaction (46, 48). This process, known as the Cyclar process, requires a much higher temperature, typically 600°C, for the reaction to occur when compared to methanol conversion at 400°C for the present study. In the propane aromatization reaction, as with the partial oxidation of methane (54), both β-Ga_2O_3 and H-ZSM-5 gave different product distributions for the separate components. β-Ga_2O_3 gave a low yield of propene, whereas over H-ZSM-5, at 600°C, propane was cracked to give CH_4 and C_2H_4. However, when combined in a simple physical mixture (48, 55) the formation of CH_4, C_2H_4, and C_3H_6 was suppressed, and benzene, toluene, and xylene were formed as the major products. Hence, although both the methane partial oxidation reaction (54) and the Cyclar process (46–48) are clear examples of contact synergy between β-Ga_2O_3 and another oxide or zeolite, there is a clear difference between the results for the methanol conversion reaction and those for these two processes. In the case of methane and propane conversion over the β-Ga_2O_3 composite catalysts, the catalyst activity and performance are totally changed, and the new observed reactions occur at a higher rate than the different observed reactions in the separate components. This is not the case for the observed effect for the methanol conversion reaction. In this case, we consider that the new site, formed at the junction between β-Ga_2O_3 and H-ZSM-5 crystallites, catalyzes a secondary reaction of a product formed initially by the acid-catalyzed conversion of methanol at sites within the zeolite crystallites. Indeed, when heptane was reacted over the β-Ga_2O_3/H-ZSM-5 physical mixture at 400°C, no difference was observed for the reaction of heptane over H-ZSM-5 alone.

A related effect of contact synergy is observed for the combination of WO_3 supported on γ-Al_2O_3 and β-Ga_2O_3. At an elevated temperature of 450°C, the formation of aromatic products is briefly observed for this catalyst. However, the major effect in this case is the enhancement in catalytic activity for the formation of methane. This is probably related to the known reactivity of β-Ga_2O_3 for the activation of C–H bonds (54), which probably enhances the donation of a hydride species from methanol to a surface methoxyl intermediate (38).

Comments on the Nature of the Active Site and the Reaction Mechanism of Aromatic Hydrocarbon Formation

As noted earlier, the present study shows that a new active site can be formed at the junction between the crystallites of β-Ga_2O_3 and H-ZSM-5 as a manifestation of contact synergy, which has been previously well documented, for other oxides (56, 57). In the physical mixture of β-Ga_2O_3/H-ZSM-5, the formation of aromatic hydrocarbons does not appear to be shape selective, since the more alkylated C_8 and C_9 aromatic compounds were the major products. Experiments using *o*-xylene as a reagent showed that the addition of β-Ga_2O_3 to H-ZSM-5 did not affect the selectivity significantly; hence, we conclude that the C_8 and C_9 aromatic products are not formed by transalkylation reactions at the new active site. The experiments using heptane, as noted previously, also confirm that alkane dehydroaromatization does not occur at 400°C. The aromatic products are formed at the expense of C_3–C_5 alkenes, and we propose that the aromatic products are formed by dimerization and dehydroaromatization of these alkenes. The active site of this reaction can be considered to be Ga^{3+} cations in Ga_2O_3 in close proximity with the Brønsted acid site of the zeolite. At this site it is possible that the activation and dimerzation of the alkenes occur via one of two routes:

1. The activation occurs at the interface between the Ga_2O_3 and the zeolite;
2. The activation initially occurs on the Ga_2O_3, and then an intermediate is transferred via the gas phase and subsequently reacted in the zeolite.

However, possibility 2 can be discounted from the experiments using separate beds of β-Ga_2O_3 and H-ZSM-5, since only when β-Ga_2O_3 and H-ZSM-5 were mixed together was the enhancement in aromatic hydrocarbon yield observed. In this case a separate bed of β-Ga_2O_3 upstream of a bed of H-ZSM-5 did not affect the catalytic performance of the zeolite markedly. Hence, it is clear that the two components must be in contact, or at least in very close proximity, to observe the effect. It is interesting to consider the nature of the intermediate that could be the precursor to the aromatic compounds. Haw and co-workers (58–61) have shown that cyclopentenyl cations can be observed in the methanol conversion reaction over H-ZSM-5 at 370°C using ^{13}C MAS NMR spectroscopy. Cyclopentenyl cations were observed to undergo extensive skeletal rearrangements including equilibration with six-membered rings and open-chain species. Haw and co-workers (58) concluded that a cyclopentenyl intermediate, formed by alkene oligomerization, could be a crucial intermediate in the methanol conversion reaction. It is also possible that these species play a key role in the formation of aromatic products in the β-Ga_2O_3/H-ZSM-5 physical mixtures. It is interesting to note that, recently, Choudhary *et al.* (62) showed that ethene can be aromatized by reaction over Ga-modified ZSM-5. In their study, the Ga species was located in the zeolite pores permitting an effective contact between the Ga and the Brønsted acid site, which is in agreement with our findings for methanol conversion. Furthermore, they observed that an optimum ratio is required between the nonframework Ga and the Brønsted acid site to observe high selectivity to aromatic hydrocarbons.

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