Characterization of Ga/ZSM-5 for the catalytic aromatization of dilute ethylene streams

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Ga/ZSM-5 is an effective catalyst for the conversion of dilute (3%) ethylene-in-methane reactant streams into aromatic hydrocarbons at 500–550 °C. A Ga loading as low as 0.5 wt% is sufficient to obtain maximum yields of aromatic products. At 520°C, an ethylene conversion of 93%, with an aromatics selectivity of 81%, was obtained over a 5 wt% Ga/ZSM-5 catalyst. The conversion of ethylene into aromatics over Ga/ZSM-5 catalysts involves a complex sequence of oligomerization, isomerization, cracking, and cyclization reactions that occur on Brønsted acid zeolites in the zeolite. The role of the gallium, which exists as both Ga^{3+} at zeolitic exchange sites and as Ga_2O_3 within the channels and on the external surface of the calcined catalyst, is to promote dehydrogenation of the acid-catalyzed oligomerization and cyclization products.

Keywords: ethylene, aromatics, Ga/ZSM-5

1. Introduction

One of the most significant problems associated with the development of a practical system for utilizing the oxidative coupling of methane (OCM) for the production of C_{2+} olefins is the economical removal of the desired ethylene product from a reactant stream that may contain a large excess of methane. In a typical bench-scale OCM recycle reactor system, for example, we have observed a steady-state C_2H_4 concentration of $\sim$3 mol%, with the balance of the recycle stream consisting largely of CH_4 and small amounts of C_2H_6 and CO_x [1]. Several investigators have reported various techniques for the separation and/or removal of diluted C_2H_4 from OCM process streams. Most of these approaches have involved condensation of the olefin onto various solid adsorbents, with subsequent recovery by thermal treatment [2–5]. We have previously described a closed-loop system in which C_2H_4 is continuously removed from an OCM recycle stream by absorption through a porous membrane into a circulating Ag^+ solution, followed by thermal decomposition of the resulting Ag^+–olefin complex and release of the gaseous olefin [1]. The practical application of all such removal techniques in an OCM reaction system, however, is limited by the need for discontinuous multiple-step operation, in the case of solid adsorbents, or by the inherently slow rate of olefin transport through the membrane, in the case of complexation processes.

An alternative approach to the physical removal and recovery of the ethylene produced during OCM processes is continuous conversion of the olefin to higher molecular weight products by an additional in-line catalytic reactor. We have previously reported, for example, the use of a Ga/ZSM-5 catalyst for converting the C_2H_4 generated in a recycle-type OCM reaction system into high yields of aromatic products [6]. Although the focus of the present research was primarily on the conversion of C_2H_4 formed during the OCM reaction, many refinery product streams contain olefins in small concentrations, and there is also a need to develop economical methods for the removal of these hydrocarbons. Several groups have previously investigated the aromatization of ethylene over various catalysts, but virtually all of these prior studies have involved the conversion of concentrated C_2H_4 feed streams, rather than the highly diluted streams typical of OCM reactors [7–11]. In the present communication, we describe in more detail the catalytic conversion of CH_4-diluted C_2H_4 streams over Ga/ZSM-5, including spectroscopic characterization of the catalyst.

2. Experimental

2.1. Catalysts

The H-ZSM-5 used for catalyst preparation was obtained by calcining NH_4-ZSM-5 (Si/Al = 25, PQ Corporation) at 550 °C for 5 h. K-ZSM-5 was prepared by ion exchange of NH_4-ZSM-5 with a 0.1 M aqueous solution of KNO_3 (Fisher) at 95 °C for 1 h, followed by extensive washing in deionized water to remove NO_3^- ions. After drying for 10 h at 120 °C, the sample was calcined at 550 °C for 5 h. Ga/ZSM-5 and Ga/K-ZSM-5 catalysts containing various loading levels of gallium were prepared by incipient wetness impregnation of NH_4-ZSM-5 or K-ZSM-5, respectively, with aqueous solutions containing the appropriate concentrations of $Ga(NO_3)_3$ (Aldrich, 99.9%). The resulting materials were dried at 120 °C for 10 h, calcined at 550 °C for 5 h, and then crushed to 20/45 mesh

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granules. 5 wt% Ga/SiO_2 was prepared by impregnating Davison Grade 57 silica gel to incipient wetness with an aqueous solution containing the appropriate concentration of $Ga(NO_3)_3$, followed by drying at 120 °C for 10 h and calcination at 550 °C for 5 h.

2.2. Catalytic reactions

All reactions were carried out using an 8 mm I.D. quartz tubular fixed-bed reactor, containing 1.0 g of the desired catalyst and 4 ml of quartz chips located prior to the catalyst bed to preheat the incoming feed gases. An electric furnace was used to heat the reactor to the desired temperature. Reactant gas flow rates were maintained by mass-flow controllers. Reaction mixtures were analyzed by gas chromatography using a TCD and a series-parallel arrangement of two packed columns: a $1/8$ in $\times$ 7 in long column containing 5% AT-2000 + 1.75% Bentone 34 on Chromasorb WNW 100/120, for separation of C_{9+} aromatics, and a $1/8$ in $\times$ 10 ft column containing HayeSep D 100/120, for separation of all other reactants and products.

2.3. Catalyst characterization

X-ray diffraction patterns were obtained using Ni-filtered Cu-Kα radiation on a Rigaku Ru-200 automated powder diffractometer equipped with a rotating anode. XPS spectra were acquired on a PHI model 5500 spectrometer employing a pass energy of 29.35 eV, a step increment of 0.125 eV, and a Mg anode power of 400 W. Samples were analyzed in the form of pressed wafers; binding energies were referenced to the C 1s line of adventitious carbon at 284.6 eV and the Si 2p line from the zeolite at 103.5 eV. Infrared spectra were obtained with a Perkin-Elmer Spectrum 2000 FT-IR spectrometer. Self-supporting pressed wafers of the catalysts were pretreated in vacuum (10^{-5} Torr) at 510 °C for 4 h, and all spectra were recorded with the sample at ambient temperature, using a resolution of 4 cm^{-1}.

3. Results and discussion

3.1. Catalyst characterizations

The effect of gallium promoter on the acid sites of the zeolite support was determined from infrared spectra in the O–H stretching region. Figure 1 shows infrared spectra of the H-ZSM-5 support and of several calcined Ga/ZSM-5 catalysts having various gallium loadings. As shown in spectrum (a), pure H-ZSM-5 contains three principal types of hydroxyl groups. One of these, having a vibrational frequency of 3611 cm^{-1} and associated with framework aluminum within the H-ZSM-5 channels, results in the strong Brønsted acidity of the zeolite [12]. The intensity of this band correlates with the aluminum content of the zeolite [13] and with the extent of proton exchange [14]. A second hydroxyl group, having a stretching frequency at 3745 cm^{-1}, has been attributed to silanol groups that terminate the zeolite lattice, i.e., those on the external surface [12,13], and are either non-acidic or only weakly acidic. The third O–H band at about 3665 cm^{-1} has been attributed to hydroxyl groups that are associated with extra-framework aluminum species [15]. A separate ^{27}Al NMR experiment confirmed the presence of a significant amount of extra-framework aluminum in this H-ZSM-5 zeolite.

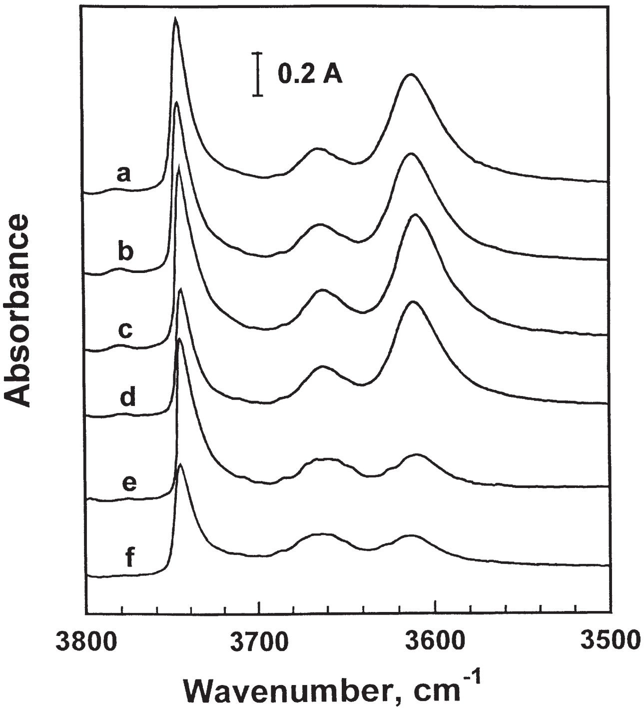

Figure 1. Infrared spectra of ZSM-5-based catalysts following calcination for 5 h at 550 °C and evacuation for 4 h at 510°C. (a) H-ZSM-5; (b) 0.1 wt% Ga/ZSM-5; (c) 0.5 wt% Ga/ZSM-5; (d) 5 wt% Ga/ZSM-5; (e) 5 wt% Ga/K-ZSM-5.

Impregnation of the zeolite with either 0.1 or 0.5 wt% Ga (spectra (b) and (c) in figure 1) resulted in essentially no change in either the intensity or the location of any of the three O–H bands. A Ga loading of 5 wt% (spectrum (d)), however, decreased the intensities of the O–H bands at 3745 and 3611 cm^{-1} by $\sim$30 and 15%, respectively, indicating that gallium in the calcined catalyst is located both within the channels of the zeolite and on its external surface. It should be noted, however, that 5 wt% of Ga corresponds to $\sim$1.2 Ga ions per Al atom in the zeolite. Thus, since each Ga^{3+} ion could, in principle, replace the H^+ ions on three O–H groups, the extent of ion exchange of H-ZSM-5 with Ga^{3+} is not extensive, and most of the gallium in the calcined catalysts presumably exists as Ga_2O_3. XPS spectra of the 5 wt% Ga/ZSM-5 catalyst in the Ga 2p and 3d regions were consistent with the presence of only Ga^{3+}, but could not be used to unambiguously distinguish between Ga ions at zeolitic exchange sites and that present as Ga_2O_3 either within the channels or on the external surface of the zeolite. XRD spectra of this catalyst, however, showed no evidence for any crystalline Ga-containing compound, indicating that the Ga_2O_3 was either in an amorphous form or was highly dispersed on the zeolite.

By contrast, ion exchange of the H-ZSM-5 with an excess of K^+ caused an 80% decrease in intensity of the band at 3611 cm^{-1} due to Brønsted O–H groups (spectrum (e)), while having virtually no effect on the O–H band at 3745 cm^{-1}. Hence, most of the K^+ in this material is located at exchange sites within the zeolite channels, with relatively little occurring on the external surface. As a result, the Brønsted acidity of the original zeolite is almost completely absent in the K-exchanged form. Subsequent impregnation of the K-ZSM-5 with 5 wt% Ga had no further effect on the 3611 cm^{-1} band (spectrum (f)), but decreased the intensity of the 3745 cm^{-1} band to approximately the same extent as in the absence of potassium (spectrum (d)), again indicating that most of the impregnated Ga in the calcined catalyst occurs on the external surface of the zeolite.

3.2. Catalytic reaction results

Results obtained for reaction of a 3 mol% C_2H_4-in-CH_4 feed stream over unpromoted H-ZSM-5 at several temperatures in the range 300–650 °C are summarized in table 1. The selectivity shown for each product is the percentage of all product C atoms that is contained in that compound. (A small amount of coke formation during each experiment accounts for the remaining product C atoms that are not included among the tabulated products.) At 300 and 400 °C, C_2H_4 conversions over H-ZSM-5 were >80%, but the principal products were C_3–C_5 alkenes and alkanes; <20% of the C_2H_4 reactant was converted to aromatic products. When the reaction temperature was increased to 520 and 650 °C, C_2H_4 conversion decreased significantly, presumably because of coke formation on the catalyst at these higher temperatures. Thus, pure H-ZSM-5 is not an effective catalyst for the conversion of a dilute ethylene stream to aromatic products.

However, the catalytic behavior of H-ZSM-5 for ethylene conversion can be improved significantly by promotion with gallium ions. Table 2 presents results for C_2H_4 reaction at 520 °C over H-ZSM-5 containing various amounts of impregnated gallium, in the range 0.1–10 wt%. It is apparent from these data that very small amounts of gallium are sufficient to cause a marked enhancement in the activity/selectivity behavior of H-ZSM-5. Even the catalyst containing only 0.1 wt% Ga had greatly increased activity and aromatics selectivity, in comparison to the pure H-ZSM-5, and 0.5 wt% Ga was sufficient to maximize both C_2H_4 conversion (at ∼91–93%) and selectivity to aromatic products (at ∼80%) at this temperature. Gallium loadings larger than 0.5 wt% resulted in essentially no additional improvement in catalytic behavior. The aromatic products consisted primarily of benzene and toluene, but also contained smaller amounts of C_{8+} aromatics, including naphthalene. The non-aromatic hydrocarbon products were principally propylene and ethane; no product contained more than three carbon atoms.

The effect of reaction temperature on the behavior of the catalyst containing 5.0 wt% Ga was investigated in the range 300–650 °C, and the results are presented in table 3. At 300 °C, although the conversion of C_2H_4 was high, the principal products were C_2–C_6 non-aromatics, with the selectivity to aromatic products being <10%. At reaction temperatures of 400–550 °C, however, the selectivity to aromatic products increased to ∼80% at C_2H_4 conversions of >90%. At 400 °C, a large amount of the aromatic products

Table 1
Effect of reaction temperature on ethylene conversion and product selectivity over H-ZSM-5.[a]

Rexn. temp. (°C)	C_2H_4 conv. (%)	Selectivity								Aromatics select. (%)	Aromatics yield (%)
		Non-aromatics			Aromatics						
		C_2	C_3	C_{4+}	Bz	Tol	C_8	C_9	Naph		
300	83	4	15	63	0	0	4	0	0	4	3
400	86	0	33	43	2	8	9	0	0	19	16
520	40	12	58	10	6	9	0	0	0	15	6
650	30	0	29	0	37	18	0	0	0	55	17

[a] 1.0 g of catalyst; $CH_4 = 100$ ml/min, $C_2H_4 = 3$ ml/min ($\tau = 1.4$ s); data taken after 70 min on stream.

Table 2
Ethylene conversion and product selectivity over Ga-containing H-ZSM-5.[a]

Ga (wt%)	C_2H_4 conv. (%)	Selectivity								Aromatics select. (%)	Aromatics yield (%)
		Non-aromatics			Aromatics						
		C_2	C_3	C_{4+}	Bz	Tol	C_8	C_9	Naph		
0.0	40	12	58	10	6	9	0	0	0	15	6
0.1	65	8	20	0	32	28	10	0	0	69	45
0.5	91	4	5	0	38	31	7	1	3	79	72
2.0	92	4	3	0	35	31	7	4	6	82	75
5.0	93	2	4	0	34	31	8	4	4	81	75
10.0	92	8	4	0	34	31	7	5	3	80	74

[a] 1.0 g of catalyst; reaction temp. = 520 °C; $CH_4 = 100$ ml/min, $C_2H_4 = 3$ ml/min ($\tau = 1.4$ s); data taken after 70 min on stream.

Table 3
Effect of reaction temperature on ethylene conversion and product selectivity over 5 wt% Ga/ZSM-5.[a]

Rexn. temp. (°C)	C_2H_4 conv. (%)	Selectivity								Aromatics select. (%)	Aromatics yield (%)
		Non-aromatics			Aromatics						
		C_2	C_3	C_{4+}	Bz	Tol	C_8	C_9	Naph		
300	89	9	14	63	3	0	6	0	0	9	8
400	91	2	9	15	12	28	32	0	0	72	66
500	94	4	4	0	34	31	7	3	3	78	73
520	93	2	4	0	34	31	8	4	4	81	75
550	93	6	1	0	35	25	5	5	10	80	74
650	54	8	2	0	40	18	1	5	6	70	38

[a] 1.0 g of catalyst; $CH_4 = 100$ ml/min, $C_2H_4 = 3$ ml/min ($\tau = 1.4$ s); data taken after 70 min on stream.

Table 4
Ethylene conversions and product selectivities in N_2 diluent.[a]

Catalyst	Contact time τ (s)	C_2H_4 conv. (%)	Selectivity									Aromatics select. (%)	Aromatics yield (%)
			Non-aromatics				Aromatics						
			C_1	C_2	C_3	C_{4+}	Bz	Tol	C_8	C_9	Naph		
H-ZSM-5	0.07	0	–	–	–	–	–	–	–	–	–	–	–
	1.4	35	3	0	63	17	8	10	3	0	0	21	7
5 wt% Ga/ZSM-5	0.07	36	tr	tr	21	7	33	29	10	0	0	72	26
	1.4	95	3	3	2	0	32	29	7	13	6	87	83
5 wt% Ga/K-ZSM-5	0.07	3	0	b	b	0	0	0	0	0	0	0	0
5 wt% Ga/SiO_2	0.07	0	–	–	–	–	–	–	–	–	–	–	–

[a] Reaction temp. = 520°C; $N_2 = 100$ ml/min, $C_2H_4 = 3$ ml/min; data taken after 70 min on stream.

[b] Approximately equal amounts of C_2 and C_3 products, but could not be determined accurately due to low C_2H_4 conversion.

(32%) consisted of C_8's, principally xylenes, but the latter decreased with further increase in reaction temperature, and at 500–550 °C, the principal aromatic products were benzene and toluene in approximately equal amounts. At 650 °C, although the aromatics selectivity remained high, conversion of C_2H_4 decreased markedly because of coke formation on the catalyst.

With increasing time-on-stream, the selectivity of the 5 wt% Ga/ZSM-5 catalyst to aromatic products remained unchanged at $\sim$80%, but the conversion of C_2H_4 and, hence, the yield of aromatics, decreased steadily. After 10 h on stream, for example, the ethylene conversion had declined from an initial value of 93% to a level of 76%, resulting in a corresponding decrease in the yield of aromatics from 74 to 59%. The original activity/selectivity behavior of the aged catalyst could, however, be fully restored by calcination in air at 500 °C for 1 h.

Due to the presence of excess methane as a diluent for the 3% C_2H_4 reactant in the reaction results presented in tables 1–3, the formation of CH_4 as a possible product of ethylene conversion could not be determined. For this reason, additional experiments were performed in which N_2 was employed as the diluent. Results obtained at 520 °C for unpromoted H-ZSM-5 and for selected Ga-containing catalysts are presented in table 4. At a contact time of 1.4 s (the same as that used for the experiments shown in tables 1–3), the overall selectivity behaviors of both unpromoted H-ZSM-5 and of 5 wt% Ga/ZSM-5 were very similar to those observed for these catalysts in the presence of CH_4 diluent (tables 1 and 3, respectively). In both cases, methane accounted for only 3% of the product carbon.

The inherently low activity of unpromoted H-ZSM-5 for C_2H_4 conversion, in comparison to that of the 5 wt% Ga/ZSM-5 catalyst, is apparent from experiments performed using a contact time of only 0.07 s, the results of which are also presented in table 4. At this low contact time, pure H-ZSM-5 displayed no measurable activity for C_2H_4 conversion, while the Ga/ZSM-5 catalyst converted 36% of the C_2H_4 reactant. In the latter case, the selectivity to aromatic products was slightly lower than at the longer contact time, and an increased amount of C_3 products was observed, suggesting their possible role as intermediates in aromatics formation. Both the Ga/K-ZSM-5 and Ga/SiO_2 catalysts were virtually inactive for C_2H_4 conversion, indicating that the zeolitic Brønsted acid sites are necessary for initial activation of the C_2H_4 reactant. Furthermore, the overall activity/selectivity behavior of a 1 : 1 physical mixture of unpromoted H-ZSM-5 and Ga/SiO_2 (not shown in table 4) was virtually identical to that of H-ZSM-5 alone, demonstrating that the Ga promoter must be in close proximity to the zeolitic acid sites to achieve optimum performance for aromatic product formation.

3.3. Reaction pathway

The selectivities shown in tables 2–4 indicate that the transformation of ethylene into aromatic products over Ga/ZSM-5 catalysts involves a complex sequence of oligomerization, cracking, isomerization, dehydrogenation,

Table 5

1-hexene and n-hexane conversions and product selectivities over ZSM-5-based catalysts in N_2 diluent.[a]

Catalyst	Reactant	Contact time τ (s)	Conv. (%)	Selectivity									Aromatics select. (%)	Aromatics yield (%)
				Non-aromatics				Aromatics						
				C_1	C_2	C_3	C_{4+}	Bz	Tol	C_8	C_9	Naph		
H-ZSM-5	1-hexene[b]	0.07	10	tr	16	44	33	1	3	3	0	0	7	1
	n-hexane[c]	0.07	23	2	18	54	27	0	0	0	0	0	0	0
		1.4	99	3	27	40	8	4	8	5	4	0	21	21
5 wt% Ga/ZSM-5	1-hexene[b]	0.07	100	1	10	31	22	6	14	16	0	0	36	36
	n-hexane[c]	0.07	51	2	15	32	21	9	11	8	3	0	31	16
		1.4	100	4	6	9	tr	20	30	20	4	4	78	78
5 wt% Ga/SiO_2	1-hexene[b]	0.07	0	–	–	–	–	–	–	–	–	–	–	–
		1.4	24	0	14	10	60	17	0	0	0	0	17	4
	n-hexane[c]	1.4	<1	0	46	54	0	0	0	0	0	0	0	0

[a] Reaction temp. = 520°C; N_2 = 100 ml/min; data taken after 70 min on stream.

[b] 1-hexene flow rate = 7 ml/min.

[c] n-hexane flow rate = 6 ml/min.

and cyclization reactions. The initial step presumably involves activation of the ethylene reactant on Brønsted acidic sites of the zeolite, followed by oligomerization reactions on these sites to produce C_4, C_6, and possibly higher hydrocarbons. These initial oligomerization products may then react further by undergoing subsequent isomerization, cracking and re-oligomerization reactions on the acid sites, resulting in the observed array of non-aromatic products. Indeed, at low contact times, both n-hexane and 1-hexene reactants, for example, produce a similar range of C_1–C_6 products over unpromoted H-ZSM-5 at 520 °C (table 5).

The presence of Ga, however, promotes extensive dehydrogenation reactions of the initial and re-oligomerized products of ethylene reaction, followed by subsequent acid-catalyzed cyclization and further Ga-promoted dehydrogenation reactions to generate the various observed aromatic products. The dehydrogenation activity of both unsupported Ga_2O_3 and of zeolite-supported Ga has been reported previously by several investigators [16–18]. The significant amounts of toluene and C_9 aromatics produced from ethylene conversion over Ga/ZSM-5 (table 4), even at low contact times, indicate that rapid cracking, isomerization, and re-oligomerization reactions, prior to dehydrogenation and aromatization, play an important role in determining the observed product distributions, since aromatics containing an odd number of C atoms cannot be formed directly from ethylene oligomerization products. The occurrence of such a multi-step reaction scheme is further demonstrated by the fact that both n-hexane and 1-hexene reactants, in addition to forming a variety of non-aromatic products, also generate significant amounts of aromatic products other than benzene over Ga/ZSM-5 (table 5). In fact, at a contact time of 1.4 s, the overall activity/selectivity behavior of 1-hexane reactant over Ga/ZSM-5 closely resembles that of ethylene (table 4). In contrast, over Ga/SiO_2, in the absence of the zeolitic acid sites, activities for conversions of the two C_6 reactants are very low, thus demonstrating the importance of the bifunctional nature of Ga/ZSM-5 in generating the observed selectivities.

4. Conclusions

This investigation has established that Ga/ZSM-5 acts as a bifunctional catalyst for the conversion of ethylene into aromatic products at 500–550 °C. Initial activation of ethylene reactant occurs on Brønsted acid sites inside the zeolite channels, leading to oligomerization reactions that generate C_4, C_6, and possibly higher hydrocarbons. The initial oligomerization products undergo a complex sequence of subsequent acid-catalyzed isomerization, cracking, re-oligomerization, and cyclization reactions that result in an array of C_1–C_6 non-aromatic products. The role of the gallium promoter is to catalyze dehydrogenation of the various acid-catalyzed oligomerization and cyclization intermediates. Following calcination, the Ga probably exists as both Ga^{3+} at zeolitic exchange sites and as Ga_2O_3 within the channels and on the external surface of the zeolite.

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