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Catalytic Conversion of Propane to Aromatics: Effects of Adding Ga and/or Pt to HZSM-5

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ZSM-5 catalysts without (H) and with added metals (Ga, PtGa, Pt) have been studied for propane conversion and aromatization at 530°C, with the contact time varied by three orders of magnitude. From initial rate and selectivity determinations, the role of the modifying metals has been ascertained. On metal-free HZSM-5 propane yields equimolar methane and ethylene as well as propylene. Adding metals increases the rate of propylene formation, as a result of their dehydrogenation activity, which acts additively rather than synergistically. The intrinsic dehydrogenation activity, observed at low conversion and time on stream, increases in the order Ga < PtGa < Pt. At higher conversion and/or longer time on stream, the reverse order is found for the formation of aromatics. It is shown that Pt but not Ga undergoes rapid coke deactivation under aromatization conditions. © 1994 Academic Press, Inc.

1. INTRODUCTION

The conversion of aliphatic compounds to aromatics is of considerable theoretical and industrial importance. The most important aromatics, benzene, toluene, and xylene (BTX), are synthesized by cyclization and dehydrogenation of paraffins and cycloparaffins of the corresponding carbon number. The catalyst in this reforming process, platinum supported on chlorided alumina, acts predominantly as a dehydrogenation catalyst. The weak acidity of the catalyst serves mainly to isomerize cyclopentanes to cyclohexanes, and paraffins to isoparaffins.

Acid-catalyzed aromatization of aliphatic hydrocarbons in the absence of metals was described by researchers at Mobil Corporation (1, 2). In this process, termed M-2 forming, paraffins from ethane to high boiling naphthas, as well as cycloparaffins, can be utilized. The key intermediates in this reaction are olefins (3). They can be used as direct feed, or produced *in situ* by cracking not only of paraffins, but of a very wide variety of other compounds such as terpenes, corn oil, and rubber latex (3–5) or alcohols, such as heptanol. Methanol is the feed in the commercial methanol-to-gasoline (MTG) process in which olefins are also the key intermediates (6).

For this acid-catalyzed aromatization, the medium pore zeolite HZSM-5 is most effective. Large pore zeolites or amorphous silica–alumina gives only a low yield of aromatics due to rapid coke formation.

Hydrogen balancing requires that aromatics of low hydrogen content be accompanied by hydrogen-rich products. With HZSM-5, this occurs via formation of light paraffins as well as a small amount of hydrogen. The hydrogen content of the feed and the nature of the paraffinic coproducts have a dominant effect on the maximum aromatic yield obtainable. This is illustrated in Table 1. The aromatic product is represented by toluene, which is the major aromatic formed at about 523°C (7). Clearly, the maximal obtainable aromatic yield is highest with feeds of lower hydrogen content, and with coproduced light paraffins of high hydrogen content such as methane. It has been found that the reaction temperature is the major variable determining the nature of the light paraffins; increasing temperature favors the lighter, more hydrogen-rich paraffins (7).

For feeds containing heteroatoms such as oxygen, the hydrogen content of the feed and the corresponding H/C ratio need to be corrected for the conversion to water (e.g., from alcohols) and/or carbon oxides (e.g., from carboxylic acids or esters). The resulting "effective H/C ratio" then determines the ultimate aromatics yield, as has been shown previously (5).

It is evident from Table 1 that H_2 is the most desirable coproduct to aromatics. The direct formation of H_2 from paraffins in acid-catalyzed dehydrogenation is now firmly established (8, 9). However, the selectivity to hydrogen is usually low. Therefore, the addition of dehydrogenation components has been investigated extensively in order to increase the rate of conversion and the ultimate yield of aromatics (10–22). Such added dehydrogenation catalysts can act on the paraffinic feed or on higher olefins and

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TABLE 1

Calculated Yield of Aromatics (as Toluene wt%) from Aliphatics wt% Hydrogen Content in Brackets

Hydrogen rejected as	Feed		
	Propane (18.2)	Hexane (16.3)	Olefin (14.3)
Propane (18.2)	—	20.0	41.1
Ethane (20)	16.1	32.9	50.5
Methane (25)	41.8	53.5	65.7
Hydrogen (100)	89.6	91.7	93.9

cycloparaffins or cycloolefins, which are reaction intermediates (3, 10, 12, 15, 23) for the formation of aromatics.

In spite of considerable research effort, no clear picture of the role of metals in the complex aromatization mechanism has emerged. Platinum, one of the most active paraffin dehydrogenation catalysts, increases the aromatics yield only modestly, if at all, when added to HZSM-5. By contrast, low activity metals such as Zn and Ga have a very beneficial effect, and Ga/HZSM-5 is the commercially preferred light paraffin aromatization catalyst in the Cyclar process.

Contradictory results have also been reported on the role of acidic and dehydrogenating components in the initial propane activation and the final stages of paraffin aromatization. According to Kitagawa *et al.* (13), Ga does not participate in the activation of propane, but catalyzes the efficient transformation of intermediates into aromatics. Gnep *et al.* (15), on the other hand, proposed that Ga promotes the rates of both propane activation and aromatics formation, whereas Mole *et al.* (12) assume that the aromatization step is catalyzed only on acidic sites. Even in the case of propane activation, the relative roles of metal and acidic sites are still uncertain. Platinum has a high activity for the dehydrogenation of paraffins but is also an active hydrogenolysis catalyst (10), while Ga is assumed to have moderate or low activity in hydrogenolysis. It is therefore of interest to examine bimetallic combinations of the two metals. Pt/Ga/ZSM-5 has been prepared by Meriaudeau *et al.* (17), who showed improved activity in the conversion of propane. In these studies, however, the activity of various catalysts is only compared at fixed conditions; the role of each component in each step of the reaction mechanism is largely unresolved.

Most of the authors seem to agree that Ga added to HZSM-5 increases the rate of hydrogen production from propane, thus increasing the rate of conversion and the aromatics selectivity. Two different mechanisms have been proposed for this. In the view of Yao *et al.* (19) and of Iglesia and co-workers (20–22), the rate of propane conversion by HZSM-5 is limited by the slow rate of desorption of H adatoms, which build up to high surface fugacities and inhibit acid-catalyzed reactions; hydrogen adatoms are removed predominantly by reaction with coadsorbed hydrocarbon fragments. Added metals such as Ga are proposed to provide a recombinative desorption function for the H adatoms (19–22) also described as hydrogen back-spillover (19, 24), thus reducing any inhibiting effect on acid-catalyzed reactions. In detailed studies it has been shown how such H adatom recombinations most likely involve a GaH_x species, possibly a hydridic hydrogen on Ga and a proton from the acidic bridging hydroxyl of the zeolite (22). The metal thus acts as a "porthole" for the exit of hydrogen generated from propane on the acid sites of the zeolite.

Other authors (15, 17, 25–27) have proposed that the added metals (Ga, Pt) play an independent, additive role as propane dehydrogenation catalysts in addition to the acid catalyst HZSM-5, the combination acting as a classical dual-functional catalyst. This view does not rule out the possibility that part of the added Ga may replace some of the zeolite protons, or that the propane dehydrogenation activity of the Ga moiety is increased by dispersion within the zeolite cavity and possibly by interaction with a proton (28) or by being in the vicinity of a proton (29). The feature distinguishing between the two viewpoints is the site at which propane "activation" occurs: at the acid zeolite site in the first case, both at Ga and at the acid site in the second. The latter viewpoint finds some support in the finding that in the absence of acidic supports gallium oxide can act as a paraffin dehydrogenating catalyst (26–29). Kazansky (26) has proposed that the dehydrogenation is initiated by a polarization of the C–H bond of the paraffin, as has been found earlier by others by ZnO.

The present paper describes propane conversion with Ga incorporated into HZSM-5 by a novel chemical vapor deposition of $GaCl_3$ (30) to form Ga/HZSM-5. It is compared with Pt/HZSM-5, with PtGa/HZSM-5 of low (L) and high (H) Ga/Pt ratios, and with metal-free HZSM-5. All reactions were carried out at 530°C. The feed contact time was varied to obtain data at various conversions and at different times on stream to assess the role of coke deposition. Detailed kinetic data have been obtained on the rate and selectivity of the initial step in propane conversion. Aromatics selectivity at high conversion has been determined at various times on stream.

2. EXPERIMENTAL

A. Catalyst Preparation

Pt/HZSM-5 was prepared by ion exchange; i.e., a dilute solution (0.1 *M*) of tetraammineplatinum nitrate ($[Pt(NH_3)_4](NO_3)_2$, Aldrich) was added dropwise to an aqueous slurry of HZSM-5 (UOP, Si/Al ratio = 20) at a pH between 5 and 6 at 80°C while the whole content was stirred. After ion exchange for 24 h, the slurry was filtered and washed with an excess amount of doubly deionized water. After drying in air at room temperature (RT), the sample was calcined under a high flow (180 cm^3/min) of oxygen (UHP grade, Linde) which was further purified by passing through a Pt/SiO_2-molecular sieve 5A trap in a packed bed quartz reactor. The calcination temperature was increased at a rate of 0.5°C/min from RT to 500°C and kept at 500°C for 2 h (standard treatment). After calcination, the sample was purged with Ar (UHP grade, Linde) for 30 min at the same flow rate. After cooling, this sample, called Pt/HZSM-5, was stored in a desiccator containing a saturated NH_4Cl solution.

Ga-containing samples were prepared by chemical vapor deposition (CVD); i.e., subliming $GaCl_3$ (99.99+%, Aldrich) into HZSM-5 or Pt/HZSM-5. Before mixing, HZSM-5 was subjected to the standard treatment and Pt/HZSM-5 samples were reduced with flowing hydrogen at 500°C for 2 h. After pretreatment, reactors were sealed tightly by closing both inlet and outlet valves of the reactors. Mixing was carried out in a glove bag under He (UHP grade, Linde) atmosphere by adding predetermined amounts of $GaCl_3$ to the substrates and by shaking the mixture. The reactors were sealed and kept in a refrigerator before sublimation. CVD was done under Ar or O_2 flow (180 cm^3/min) while the temperature was increased from RT to 200°C at a rate of 0.25°C/min. After 2 h at 200°C, heating is resumed to 500°C and held for 2 h at 500°C. Three samples were prepared by CVD and named Ga/HZSM-5, PtGa/HZSM-5(L), and PtGa/HZSM-5(H), respectively, where L and H stand for Ga to Pt ratio. Metal loadings are 4.25% Pt for all Pt-containing catalysts, and 0.70%, 1.88%, and 1.36% Ga for PtGa/HZSM-5(L), PtGa/HZSM-5(H), and Ga/HZSM-5, respectively.

Detailed characterization studies of a series of Ga/HZSM-5 samples prepared by the same technique have been carried out. These experiments have been described separately (30, 31).

B. Propane Conversion

Propane aromatization was carried out at atmospheric pressure in a plug flow reactor. Space velocity was varied from 3 to 8600 h^{-1} (WHSV) and the temperature was set at 530°C. An equimolar mixture of propane and Ar was used as the feed. Reaction products were analyzed by an on-line Hewlett–Packard 5890 II gas chromatograph equipped with a flame ionization detector and a thermal conductivity detector. For the analysis of hydrocarbons, a 50-m fused silica PLOT KCl/Al_2O_3 was used.

Before tests, Ga/HZSM-5 samples were calcined under O_2 flow (1 h) and reduced with H_2 (2 h) at 580°C. All other samples were pretreated at 500°C. Reaction products were analyzed at 10 min on stream for mechanistic studies, and at 10, 70, 130, 190, and 250 min on stream for deactivation studies.

3. RESULTS AND DISCUSSION

A. Rate of Propane Conversion and Product Formation

Figure 1 shows the effect of contact time (τ = W/F) on propane conversion over HZSM-5 and modified ZSM-5 catalysts at 530°C. In order to assess the intrinsic activity of various catalysts minimally disturbed by coke deposition, data were collected at only 10 min on stream for each contact time. The addition of metal increases the rate of propane conversion in the order: HZSM-5 < Ga/ZSM-5 < PtGa/ZSM-5(H) < PtGa/ZSM-5(L) ≪ Pt/ZSM-5. This result is contrary to that of Kitagawa (13), but agrees with the findings of Gnep *et al.* (15) and of Iglesia and Baumgartner (32) for the addition of Ga to HZSM-5. In our experiments, Pt has the largest rate-enhancing effect, with the Pt–Ga containing catalysts falling between Pt and Ga. The initial slopes of the conversion–contact time plots were used to determine the initial rates of propane conversion for the various catalysts. The results are collected in Table 2, column 2. The relative rates for the H, Ga, PtGa, and Pt forms of the HZSM-5 catalyst are comparable to those reported by Meriaudeau *et al.* (17), although our Pt catalyst was about 21 times more active than the hydrogen form vs a factor of 9 in Ref. (17).

Plots of molar yields of the products as a function of contact time are shown in Figs. 2a–2e. For HZSM-5 (Fig.

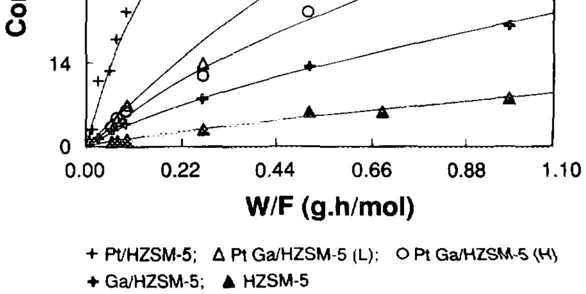


FIG. 1. Propane conversion as a function of contact time τ = W/F.

TABLE 2

Initial Propane Conversion Rates and Product Selectivities

Sample[a]	Initial rate		Initial selectivities mol%			Fract. conv. via		Initial rate m mol/g hr		Relative rates	
	m mol/g hr	relative	C_1	C_2^{2-}	C_3^{2-}	Path (a)	Path (b)	Path (a)	Path (b)	Path (a)	Path (b)
(1)	(2)		(3)			(4)		(5)		(6)	(7)
H	5.8	1.0	40	37	23	0.63	0.37	3.65	2.15	1.0	1.0
Ga	20.5	3.5	16	16	68	0.19	0.81	3.90	16.6	1.07	7.7
Pt Ga(H)	31.5	5.4	14	16	70	0.18	0.82	5.67	25.8	1.55	12
PtGa(L)	35.2	6.0	18	16	66	0.20	0.80	7.04	28.2	1.93	13.1
Pt	121	20.9	5	5	90	0.05	0.95	6.05	115	1.66	54.5

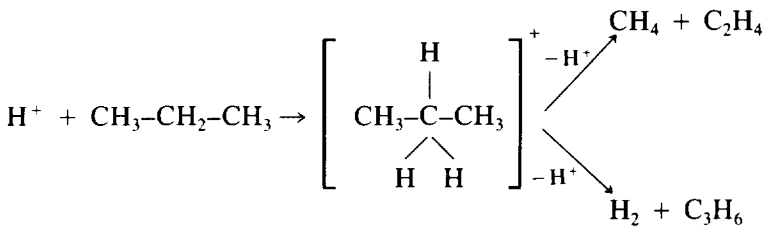
[a] H = HSZM-5, Ga = Ga/HSZM-5, PtGa(H) = PtGa/HZSM-5(H), PtGa(L) = PtGa/HZSM-5(L), Pt = Pt/HZSM-5.

2a), methane, ethylene, and propylene are clearly primary products, while ethane is a minor secondary product. With the metal-containing catalysts, (Figs. 2b–2e), a more complicated yield pattern is apparent. Ethane is formed in significant amounts at longer contact times, and consecutive reactions of the primary products are occurring rapidly.

B. Low Propane Conversion—The Initial Step

In order to obtain more precise data on initial product distributions and product formation rates, selectivity vs conversion plots were obtained (Figs. 3a–3e). Extrapolation of the selectivities to zero conversion yields initial product selectivities, which are listed in Table 2, column 3. In all cases, the only primary hydrocarbon products are methane, ethylene, and propylene. Hydrogen was not measured in this study. It is apparent that, within experimental accuracy, methane and ethylene are formed in equimolar quantities, and the proportion of propylene in the product increases upon addition of Ga and especially of Pt.

For HZSM-5, the results are completely consistent with acid-catalyzed cracking of propane by the monomolecular reaction path via pentacoordinated carbonium ions discussed earlier for hexane (8) and butane (9). In the latter reference, hydrogen was measured and found to be produced in equimolar amounts to butene at low conversion. Thus, the following mechanism is applicable:

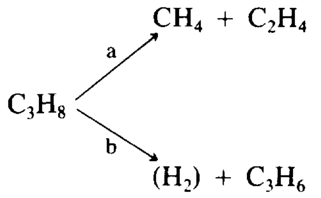


[1a]

[1b]

The depiction of the protonated propane as a pentacoordinated carbonium ion could be taken as a formalism and may well represent a combination of molecules with protonated carbon–carbon and carbon–hydrogen sigma bonds (three-center two-electron bonds). From the initial selectivities (Table 2, column 3), and an average value of (40 + 37)/2 = 38.5 for path [1a] and 23 for path [1b], we calculate that the decomposition of the protonated propane on HZSM-5 occurs to 63% by path [1a] and to 37% by path [1b]. (Table 2, column 4). The same ratio can be inferred from the data of Guisnet *et al.* (23, 33) since in both cases methane is produced with a selectivity of about 24 wt%.

With the metal-modified ZSM-5 catalysts, the initial products contain more propylene and less methane and ethylene than with the unmodified HZSM-5. In order to elucidate the reason for this selectivity change, we have obtained values for the absolute (Table 2, column 5) and relative rates (Table 2, columns 6 and 7) of product formation according to reaction paths a and b:



[2]

It is apparent from Table 2, column 6, that the addition of Ga to HZSM-5 has essentially no effect on the rate of path a, but increases the propane dehydrogenation rate 7.7-fold (column 7). A similar conclusion can be drawn

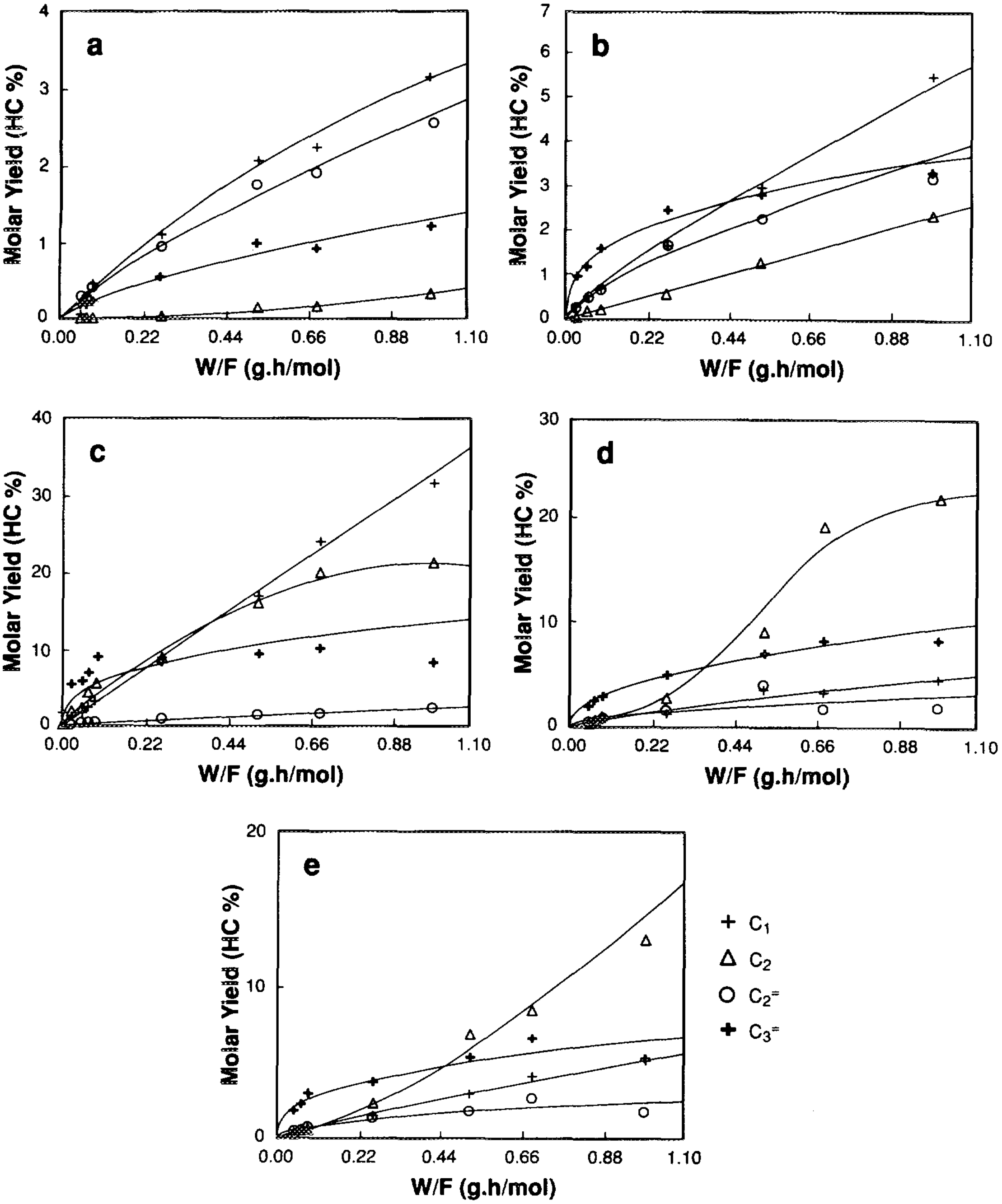


FIG. 2. Effect of contact time on product yields: (a) HZSM-5, (b) Ga/HZSM-5, (c) Pt/HZSM-5, (d) PtGa/HZSM-5(L), (e) PtGa/HZSM-5(H).

for the Pt-containing catalysts. Pt alone increased the dehydrogenation activity 54-fold (path b, column 7) but again has only a minor effect on the cracking to methane and ethylene (path a, column 6). The PtGa catalysts have decreased dehydrogenation activity, consistent with Pt–Ga interaction. It is therefore possible to describe the propane conversion over metal-modified ZSM-5 as follows:

HZSM-5: $C_3H_8 \rightarrow CH_4 + C_2H_4$ [3a]

HZSM-5: $C_3H_8 \rightarrow H_2 + C_3H_6$ [3b1]

Ga, PtGa, Pt: $C_3H_8 \longrightarrow H_2 + C_3H_6$ [3b2]

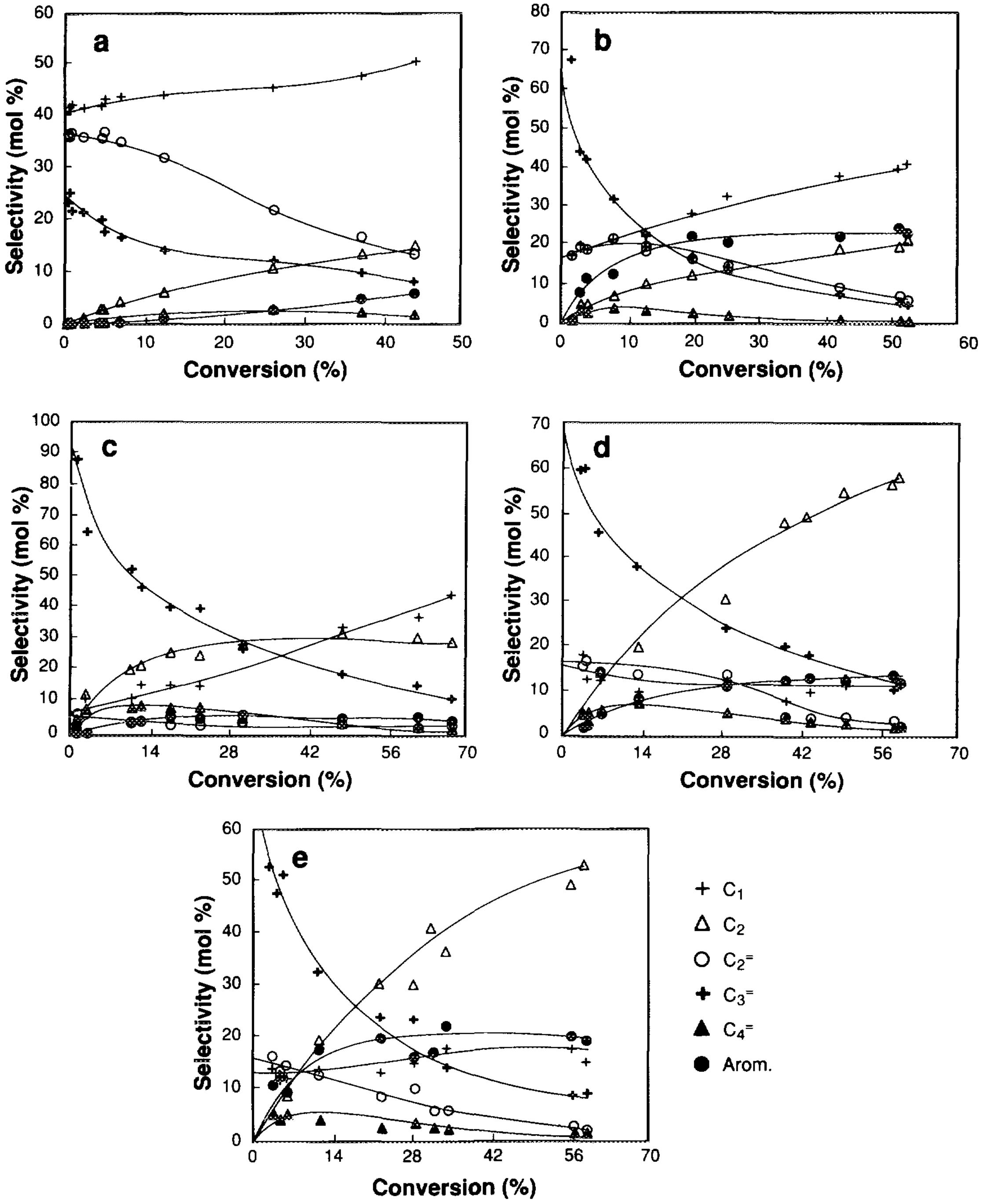


FIG. 3. Effect of conversion on product selectivities: (a) HZSM-5, (b) Ga/HZSM-5, (c) Pt/HZSM-5, (d) PtGa/HZSM-5(L), (e) PtGa/HZSM-5(H).

The metals provide an additional dehydrogenation path (3 b2), without significantly affecting the rate of the acid-catalyzed conversion (3 a, b1). Ga appears as a less active dehydrogenation catalyst relative to Pt. Since methane and ethylene are produced in equimolar amounts (Table 2, column 3), there is no evidence that the metals perform any hydrogenolysis to form methane at the initial stages of propane conversion. With our samples the metals do not suppress or modify the acid-catalyzed cracking of propane, as reported by others (12, 13).

We find that the addition of metals, i.e., Ga, Pt, and their mixtures, to HZSM-5 has little effect on its acid activity, as indicated by the similar rates of cracking propane to equimolar amounts of methane and ethylene (Table 2, columns 5a and 6). A very similar conclusion was reached by Meitzner *et al.* (22), who found that neither the acid site density nor the acid strength was significantly changed upon addition of Ga followed by reduction, as judged from the activity and selectivity of isomerization of 2-methyl-2-pentene. We suggest that with the relatively low (1.36%) Ga content of our sample, only a small fraction of the protonic sites have been replaced by cationic gallium species. With higher Ga loading, a definite decrease of the acid activity has been observed (31). The kinetic data obtained with our catalyst do not support the suggestion (21, 22) that metals such as Ga or Zn catalyze the rate-limiting removal of H adatoms as H_2 from zeolite surfaces or otherwise affect the selectivity of reactions occurring on the acid site. Obviously, by themselves they are not sufficient to disprove this suggestion either.

C. Higher Propane Conversion– The Aromatization Step

With increasing contact time $\tau = W/F$ (Fig. 2), the primary products are subject to secondary reactions. Methane, a stable product, increases nearly linearly with τ, whereas the olefins, ethylene and propylene, are highly reactive (Figs. 2 and 3) and undergo rapid further reaction. One of these is the acid-catalyzed olefin interconversion (3) which produces a thermodynamic equilibrium mixture of olefins. At low total olefin partial pressure (low conversion), this equilibrium favors ethylene.

With increasing conversion, the hydrogen concentration in the reactor increases as a result of reaction [3 b], and olefin hydrogenation can occur. We suggest that this is the major source for ethane. With HZSM-5, the hydrogenation activity is clearly evident, but low. It increases for the Ga- and especially the Pt-containing catalysts, as expected.

At higher conversion and hence olefin partial pressure, the olefin interconversion reaction produces increasing equilibrium quantities of higher olefins. These can undergo acid-catalyzed cyclization and hydride transfer reactions as well as metal-catalyzed dehydrogenations to form aromatics. These reactions have been discussed in detail previously (17, 23, 34).

Based on the hydrogen balancing considerations discussed earlier and exemplified in Table 1, a catalyst with a high dehydrogenation vs cracking selectivity should produce the highest aromatics yield. On the basis of the results in Table 2, column 3, one might expect increasing aromatics formed in the sequence HZSM-5 < Ga/HZSM-5 < Pt/HZSM-5. However, the data in Fig. 3 and Table 3 show that much larger amounts of aromatics are produced with the Ga- and PtGa-containing samples than with Pt/HZSM-5. At 40% propane conversion, the latter produces only about as much aromatics as the metal-free HZSM-5. Although all these data were obtained with relatively fresh catalyst at only 10 min on stream, it is suggested that deactivation by coking has already occurred on Pt, but not on Ga. The source of the coke is most likely 5-membered naphthenes formed by acid-catalyzed cyclization of dienes.

TABLE 3

Aromatics Selectivity at Various Propane Conversions

Sample	Aromatics selectivity (mol%) at propane conversions of 10%	20%	40%
H	0.5	1.5	5
Ga	17	20	22
PtGa(H)	15	18	20
PtGa(L)	6	9	13
Pt	3	4	6

This conclusion comes from a number of observations: (i) At short contact time, where only low molecular weight olefins and paraffins are present, platinum is the most active metal (Table 2 columns 5 and 7); (ii) Separate experiments showed that little aging of Pt on silica occurs in the conversion of cyclohexane to benzene, i.e., in the absence of an acidic component. The addition of HZSM-5 to Pt/SiO_2 led however to rapid deactivation of Pt, due to isomerization of the intermediate, cyclohexene, to methylcyclopentene; (iii) alternatively, adding 5% methylcyclopentane to cyclohexane caused rapid aging of nonacidic Pt/SiO_2. Thus, under low hydrogen pressure conditions, platinum is rapidly deactivated by added or *in situ*-generated methylcyclopentane and its dehydrogenation products, methylcyclopentene and methylcyclopentadiene. Significantly, a feed of 5% methylcyclopentane in cyclohexane did not cause deactivation of Ga_2O_3 and ZnO catalysts. Thus, these two metals are not readily deactivated by 5-membered naphthenes. This observation provides a rationale for the general finding that, in the aromatization of paraffins and olefins by ZSM-5, high aromatics yields are obtained with the addition of Zn or Ga, but not of noble metals, as reflected in the choice of Ga as an additive to HZSM-5 in the commercial Cyclar process.

In order to assess catalyst deactivation further, propane was passed over the various catalysts at low conversion which was chosen by adjusting the contact time to be initially about the same. The results in Fig. 4 show that Pt is deactivated with time on stream, whereas HZSM-5

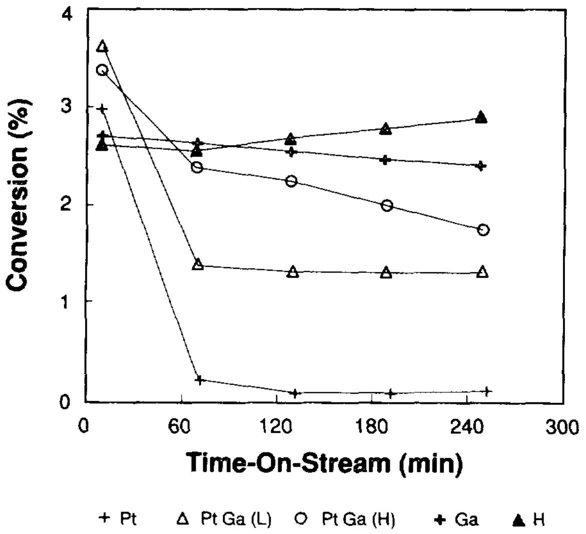


FIG. 4. Time-on-Stream dependence of propane conversion.

and Ga/HZSM-5 are not. Adding Ga to Pt reduces the deactivation in proportion to the amount of Ga added.

These observations provide an explanation for the unexpected finding that Pt added to HZSM-5 greatly increases the rate of the first step, propane conversion, but has little or no effect on the aromatization rate and selectivity.

4. CONCLUSION

In experiments at a constant temperature of 530°C, the propane conversion was varied widely by changing the WHSV from 3 to 8600. With data all taken on fresh catalysts (10 min on stream), we find that

1. The relative rate of initial propane conversion increases in the sequence H $<$ Ga $<$ PtGa(H) $<$ PtGa(L) $\leqslant$ Pt. Since the last three samples contain the same amount of Pt, strong Pt-Ga interaction and reduced activity of the Pt–Ga mixtures relative to Pt is indicated, in agreement with data by Meriaudeau *et al.*

2. The only primary hydrocarbon products from all catalysts are methane and ethylene (equimolar), and propylene, consistent with acid-catalyzed protolysis and metal-catalyzed propane dehydrogenation, the latter increasing in the sequence listed above.

3. The initial rates of forming the individual products indicate that the rate of the acid-catalyzed formation of methane and ethylene are essentially unaffected by the added metals. Thus, the acid and the metal functions appear to act merely additively as dual-functional catalysts rather than synergistically, in agreement with many but not all opinions expressed in the literature.

4. At higher conversion, ethane is formed in yields which exceed that of methane and which increase with the hydrogenation activity of the metal components. Thus, ethane does not result from propane hydrogenolysis, but from the hydrogenation of ethylene produced by protolytic cracking of propane and by olefin interconversion from propylene.

5. At the same short time on stream (10 min) but with increasing conversion, Pt and to a much smaller extent the Pt–Ga mixtures are progressively deactivated due to coke build-up. The Ga-containing and the metal-free HZSM-5 are much more resistant to deactivation. The same conclusion can be made from very low conversion data, when the conversion is followed as a function of time-on-stream.

6. These data and auxiliary observations suggest that Pt and Pt-Ga combination are little deactivated by light paraffins or olefins, but by cyclopentenes and cyclopentadienes formed as reaction intermediates in the reaction sequence which leads to aromatics formation. In spite of its intrinsically high stoichiometrically desirable dehydrogenation activity, Pt is therefore not a suitable promoter of HZSM-5 in aromatization reactions, but Ga is.

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