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Catalytic deoxygenation of benzaldehyde over gallium-modified ZSM-5 zeolite

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ABSTRACT

The deoxygenation of benzaldehyde has been investigated over gallium-modified ZSM-5 catalysts. In the absence of H_2, Ga/HZSM-5 catalyzes benzaldehyde decarbonylation resulting in benzene and CO. The active sites for this reaction are the strong Brønsted acid sites. In the presence of H_2, the main product is toluene. It is believed that Ga cationic species (Ga^+/GaH_2^+) generated during H_2 reduction can promote the hydrogenation/hydrogenolysis reactions that give toluene and water. In the absence of H_2, toluene can only be observed in transient experiments when the Ga/HZSM-5 catalysts are reduced. It is suggested that the GaH_2^+ species generated under H_2 play an important role in the hydrogenation/hydrogenolysis. However, they readily decompose to Ga^+ in the absence of H_2. The addition of water to the feed modifies the catalytic activity and selectivity of Ga/HZSM-5 catalysts. On the one hand, water generates additional Brønsted acid sites from the reaction of extra-framework Ga with chemisorbed water (GaO(OH)) and with defect hydroxyls of the zeolite framework (GaOHSi). These additional sites enhance the production of benzene but decrease the production of toluene, due to a decrease in the density of reduced Ga cationic species.

1. Introduction

Fast pyrolysis has become an increasingly attractive process for converting biomass into fuels and chemicals [1–7]. However, it is well known that the resulting pyrolysis oil product contains different types of oxygen functionalities that make it unacceptable as a transportation fuel component. One of the potential solutions that have been proposed to stabilize the pyrolysis oil and reduce its oxygen content is to blend it with the feed of conventional hydrotreating processes [8], but the storage and transportation of untreated pyrolysis oil before it can be blended are still serious complications [9]. Another alternative is to post-treat the vapors of the pyrolysis product in the same plant, before the vapors even condense into an unstable liquid [10]. In this case, the selection of catalysts does not need to be limited to those that are typically used in hydrotreating processes, which have been optimally designed to treat other types of molecules from those present in pyrolysis oil. As an initial step in the investigation of potential catalysts and processes, model compound studies provide important fundamental knowledge about reaction pathways and can provide direction in the selection of catalysts. Since aldehydes are among the most unwanted components [11–13], we have chosen to investigate the conversion of benzaldehyde, a model compound representing aromatic aldehydes in bio-oil, to oxygen-free compounds. In previous studies [14–21], metal catalysts such as Ni, Pt, Pd, and Cu have been used for hydrogenation of carbonyl compounds. Transition metals are highly active in reactions involving carbonyl compounds and hydrogen, including decarbonylation, hydrogenation, and hydrogenolysis. An alternative family of catalysts that can promote some of these reactions is that of Ga-containing zeolites. These catalysts have shown to exhibit high activity toward reactions involving activation of light alkanes, most notably aromatization [22–27]. On these catalysts, gallium may be present in different forms. It can be present as gallium oxide either in aggregated form on the external zeolite surface or as small particles occluded in the zeolite micropores. It can also be stabilized in cationic form as either oxidic GaO^+ or reduced Ga^+ and GaH_2^+ species [28–32].

In this work, we investigate Ga-based catalysts for the deoxygenation of benzaldehyde to produce oxygen-free aromatics. Reduced Ga cationic species are expected to be active for hydrogenation of carbonyl compound to alcohol and even hydrogenolysis of the C–O bond. In particular, we report the conversion of benzaldehyde on Ga/HZSM-5 catalysts. The effect of varying reaction conditions such as carrier gas (H_2 or He), reaction temperature, and water co-feeding has been investigated in a continuous flow system. Temperature-programed transient techniques were employed to investigate the possible reaction pathways.

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2. Experimental

2.1. Catalyst preparation and characterization

HZSM-5 (Si/Al ~ 45) zeolites were obtained from Sud-Chemie. Conventional impregnation of HZSM-5 with $Ga(NO_3)_3$ was employed to obtain Ga loadings varying from 1 to 6 wt% [33,34]. The impregnated samples were calcined at 550 °C for 4 h in a flow of dry air. Hereafter, the catalysts will be designated according to their wt% Ga loading as xx-Ga/HZSM-5. In addition, a 3 wt% Ga/SiO_2 sample was prepared by impregnating silica (Hi-Sil from PPG) support with $Ga(NO_3)_3$ to have as a comparison a support without acidity.

Temperature-programed reduction (TPR) experiments were carried out using a TCD detector. Prior to the H_2-TPR, each sample was heated to 550 °C in a dry air for 1 h (30 mL/min) and cooled to 50 °C. The H_2 consumption was recorded as a function temperature as the catalyst sample was heated in a flow of 2% H_2/Ar (30 mL/min) at a heating rate of 10 °C/min.

The Gorte's method [35] of *i*-propylamine TPD was used to determine the density of Brønsted acid sites. First, 50 mg of sample was pretreated at 550 °C in a flow of He. To study the variation of Brønsted acid site density after the reduction and/or steaming treatments the Ga/HZSM-5 catalysts were pretreated at 550 °C in a flow of H_2 for 2 h and at 450 °C in a flow of 0.6% H_2O/He for 2 h, respectively. After each pretreatment, the sample was cooled in He to room temperature and then pulses of *i*-propylamine (IPA) were injected until saturation. The excess IPA was removed by flowing He. When a constant background signal was obtained, the sample was heated to 900 °C at a heating rate of 10 °C/min. The mass peaks used to identify the various desorption products in IPA-TPD are as follows: $m/z = 44$ for *i*-propylamine, $m/z = 41$ for propylene, and $m/z = 17$ for ammonia. The amount of desorbed products was calibrated with 2 mL pulses of 2% propylene in He. The desorption peaks for ammonia are always broader, due to re-adsorption, but the propylene peaks are rather sharp. Therefore, as previously proposed [35], the density of Brønsted acid sites was calculated from the moles of the desorbed propylene.

The H/D exchange from gas-phase H_2/D_2 was studied using an MS detector. The catalyst sample was first heated in a flow of H_2 ($m/z = 2$) at 450–550 °C. Several consecutive 2 mL pulses of pure deuterium, D_2 ($m/z = 4$), were injected onto the sample in the H_2 carrier gas. The evolution of masses were monitored to determine the formation of H–D ($m/z = 3$).

2.2. Temperature-programed desorption (TPD) of adsorbed benzaldehyde and decomposition products

The evolution of the products resulting from pre-adsorbed benzaldehyde over modified HZSM-5 catalysts as a function of temperature was followed by mass spectrometry. Before adsorbing benzaldehyde, the sample (50 mg) was dried in a flow of carrier gas (He or H_2) at 550 °C for 2 h. Benzaldehyde was added in pulses at 180 °C until saturation was reached; then, the sample was flushed with He (or H_2) at the same temperature for 3 h and a heating ramp was initiated at a rate of 10 °C/min up to 900 °C, using He (or H_2) as the carrier gas. The masses (m/z) of 15, 18, 28, 77, 91, and 105 were monitored to determine the evolution of methane, water, carbon monoxide, benzene, toluene, and benzaldehyde, respectively.

2.3. Benzaldehyde pulse reaction

To study the interaction of benzaldehyde with the clean catalyst surface small benzaldehyde pulses were sent over the fresh zeolites. In each measurement, 50 mg of catalyst was pretreated in a flow of He or H_2 (30 mL/min) and subsequently 1 μL pulses of pure liquid benzaldehyde were vaporized over the pretreated catalyst. The same procedure was repeated at different temperatures. The products of the pulse reaction were analyzed by the MS detector, in a manner similar to that used in the TPD experiments.

2.4. Benzaldehyde conversion in a continuous flow reactor

Gas-phase catalytic conversion of benzaldehyde was investigated in a continuous fixed bed reactor. In each run, benzaldehyde vapor saturated of at 20 °C was carried over the catalyst by a 30 mL/min flow of He (or H_2). The catalyst bed was placed in a quartz tube reactor that was located inside a temperature-controlled electric furnace. The products were periodically collected and analyzed by online gas chromatography (GC). The reaction conditions were as follows: temperature, 400–550 °C; total pressure, 1 atm; carrier gas, He or H_2; weight time (W/F), 25–150 g h/mol. To investigate the effect of water in the feed, water was continuously vaporized into the reactor inlet at a flow rate of 2 mL(*liq*)/h using a syringe pump.

3. Results

3.1. Catalysts characterization

The characteristics of the catalyst samples including Si/Al ratio of the host zeolite, wt% Ga loading, and BET surface areas are summarized in Table 1.

Fig. 1 shows the TPR profiles obtained on the calcined catalyst samples. Three major peaks are observed on the Ga-modified zeolites. The contributions to the H_2 consumption from each reduction

Table 1
Chemical composition and surface area of the catalyst samples.

Catalyst	Si/Al	Ga content[a] (wt%)	Surface area (m^2/g)
HZSM-5	45	–	545
1Ga/HZSM-5	45	0.9	520
3Ga/HZSM-5	45	2.8	510
6Ga/HZSM-5	45	5.8	500
3Ga/SiO_2	–	2.9	370

[a] Elemental analysis of Si, Al, and Ga done by ICP.

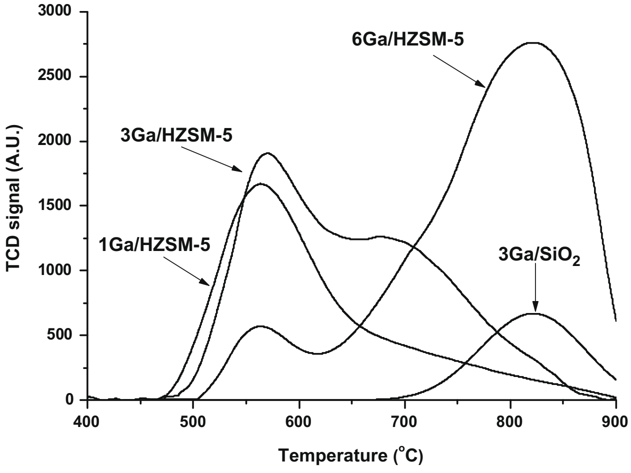


Fig. 1. TPR profiles for the catalysts 1Ga/HZSM-5, 3Ga/HZSM-5, 6Ga/HZSM-5, and 3Ga/SiO_2. The samples were first calcined at 550 °C and cooled down to 50 °C in air; then, heated in a flow of 2% H_2/Ar (30 mL/min) with a heating rate of 10 °C/min up to 900 °C.

Table 2
Summary of the temperature-programed reduction results. Peak position and hydrogen consumption for the catalyst series.

Catalyst	Temperature (°C)			% Area of H_2 consumption			H_2 uptake per Ga_2O_3 (mol ratio)
	T_1	T_2	T_3	A_1	A_2	A_3	
1Ga/HZSM-5	553	602	706	43	26	31	1.25
3Ga/HZSM-5	566	660	761	32	51	17	0.61
6Ga/HZSM-5	570	760	838	9	53	38	0.43
3Ga/SiO_2	–	–	820	0	0	100	0.13

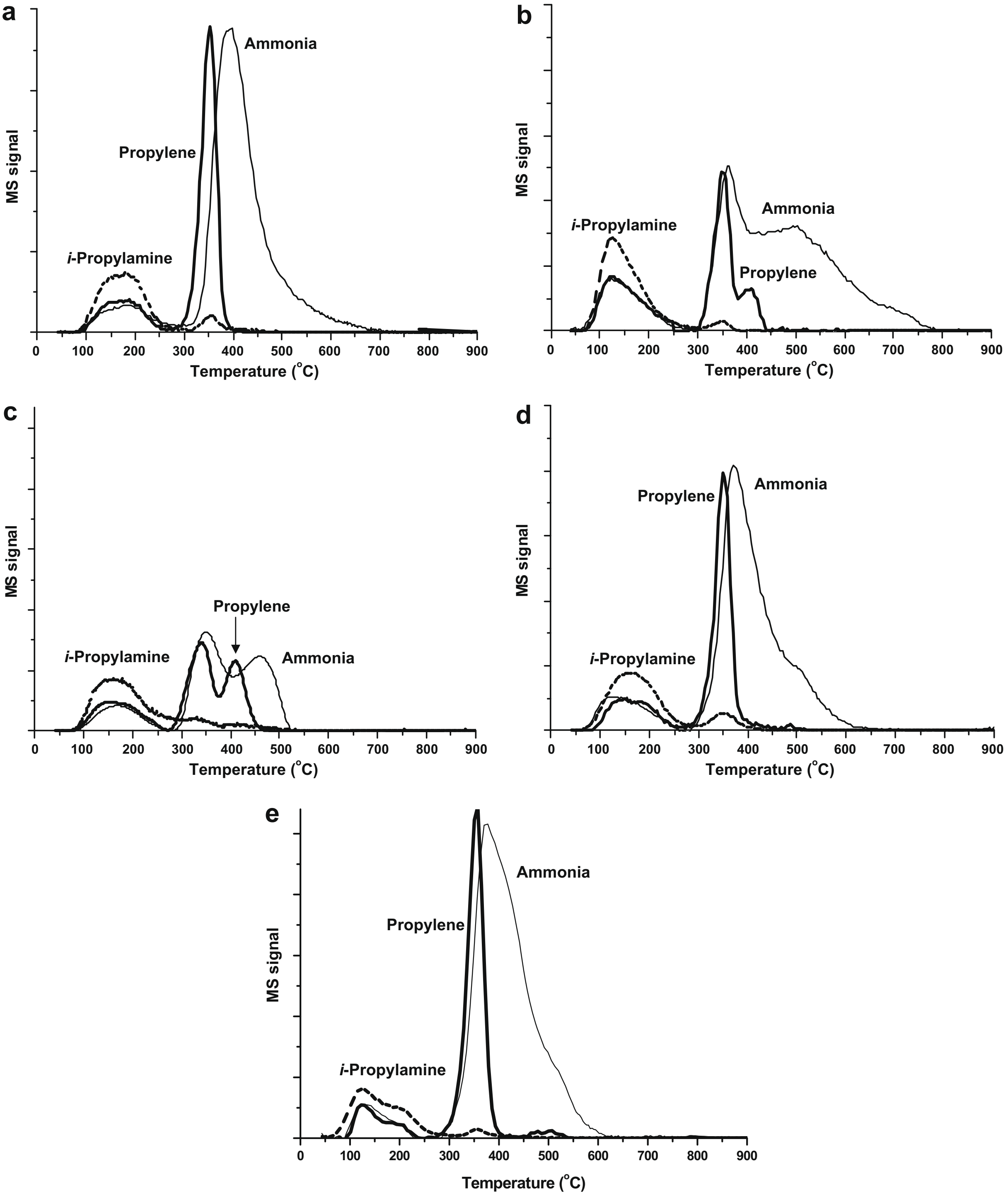


Fig. 2. Temperature-programed desorption of adsorbed isopropylamine (IPA-TPD) (a) HZSM-5, (b) red-1Ga/HZSM-5, (c) red-3Ga/HZSM-5, (d) 3Ga/HZSM-5b, and (e) st-3Ga/HZSM-5. The different pretreatments were as follows: For (a) and (d): heating in He at 550 °C for 2 h and cooling down in He. For (b) and (c), (i.e. red): heating in H_2 at 550 °C for 2 h and cooling down in He. For (e), (i.e. st): heating in steam at 450 °C for 2 h and cooling down in He.

peak, as calculated from Gaussian deconvolution, are summarized in Table 2. In the case of the 1Ga/ and 3Ga/HZSM-5 samples, the first ($T_1 \sim 550$–560 °C) and second ($T_2 \sim 600$–660 °C) peaks can be assigned to the reduction of well-dispersed Ga species such as small Ga_2O_3 particles and GaO^+ species interacting with the zeolite. The third peak ($T_3 \sim 700$–760 °C) can be attributed to larger Ga_2O_3 particles, either separated from or weakly interacting with the zeolite matrix [36]. When increasing Ga content up to 6 wt%, it is observed that the T_2 and T_3 peaks shift to higher temperatures. This shift indicates that the well-dispersed Ga species begin to agglomerate at higher loading into larger Ga_2O_3 clusters, and are probably segregated to the outer surface of ZSM-5. This migration is related to a rather weak interaction of Ga species in excess of the stabilization capacity of the zeolites matrix, which has a rather limited Al content (Si/Al = 45). In agreement with these assignments, the TPR profile of the $3Ga/SiO_2$ sample displays only one reduction peak corresponding to larger gallium oxide particles and appearing at relatively high reduction temperatures. It is indeed expected that without a uniform network of small pores or high acid strength, the silica support cannot stabilize small Ga clusters or GaO^+ species effectively. As seen in Table 2, the largest extent of H_2 consumption (H_2/Ga_2O_3) is obtained with the 1Ga/HZSM-5 sample. Consistent with the previous reports [26], the H_2 uptake decreases with increasing Ga loadings since the larger the Ga_2O_3 clusters are, the lower the extent of reduction can be achieved [37,38]. Accordingly, a high H_2 uptake was observed for the highly dispersed Ga species in the 1Ga/HZSM-5 sample that reduced at low temperatures. As discussed below, the higher reducibility of these species has an important effect on catalyst selectivity.

The second important characteristic of these catalysts that greatly influences their performance is their acid site density and distribution. Fig. 2 shows the TPD profiles of adsorbed *i*-propylamine, a well-established method [35] that allows us to quantify the number of strong Brønsted acid sites able to catalyze the Hofmann elimination reaction of *i*-propylamine. The quantification of the strong acid sites is done by monitoring the evolution of ammonia and propylene taking place at around 350 °C. The results are summarized in Table 3. It can be seen that when 3 wt% Ga was impregnated onto the HZSM-5 zeolite (3Ga/HZSM-5), only a slight reduction in the density of strong acid sites is observed. That is, when the catalyst is calcined and only heated in He, the Ga incorporated is mostly retained in the form of isolated oxide clusters (i.e. Ga_2O_3) without affecting the acid density to any significant extent. However, a significant decrease in Brønsted acid site density was observed when the catalyst was treated in H_2 (i.e. samples red-1Ga/HZSM-5 and red-3Ga/HZSM-5). This significant loss in acid site density indicates that under reducing conditions the Ga species can become exchangeable cations (i.e. Ga^+). In fact, the decrease in the strong acid sites followed the order 3Ga/HZSM-5 > 1Ga/HZSM-5 > HZSM-5 when the catalyst was reduced in H_2.

Table 3
Acidity of the various catalysts investigated.[a]

Catalyst	Acidity of catalyst (micromoles/g)		
	Strong acid sites	Weak acid sites	Total acidity
HZSM-5	315	0	315 (330[b])
3Ga/HZSM-5	305	0	305
red-1Ga/HZSM-5	149	31	180
red-3Ga/HZSM-5	91	64	155
st-3Ga/HZSM-5	377	0	377

[a] The data were summarized from IPA-TPD curves. red-1Ga/HZSM-5 and red-3Ga/HZSM-5 indicate samples reduced in H_2 flow; and st-3Ga/HZSM-5 indicates a sample steamed.

[b] Theoretical acidity, calculated from the Si/Al ratio.

In addition to the decrease in the number of strong acid sites, the introduction of Ga into the zeolite during reduction can provide additional sites with relatively lower acid strength. They need higher temperatures to start the elimination reaction and, as a result, a clearly separated propylene peak is observed for these catalysts above 400 °C. These less active sites may be assigned to GaOH species, which have been previously observed by FTIR after reduction of Ga/HZSM-5 in H_2 [32,39]. Accordingly, no propylene signal at >400 °C can be observed over 3Ga/HZSM-5 treated with He, but a high-temperature propylene peak is seen after treatment in H_2 [40].

When the Ga-containing zeolite was subjected to steaming (st-3Ga/HZSM-5), the density of strong Brønsted acid sites markedly increased (Fig. 2e) and became even higher than the parent HZSM-5 zeolite. This is consistent with the previous work of some of us [41] that shows that under steaming conditions the Ga spe-

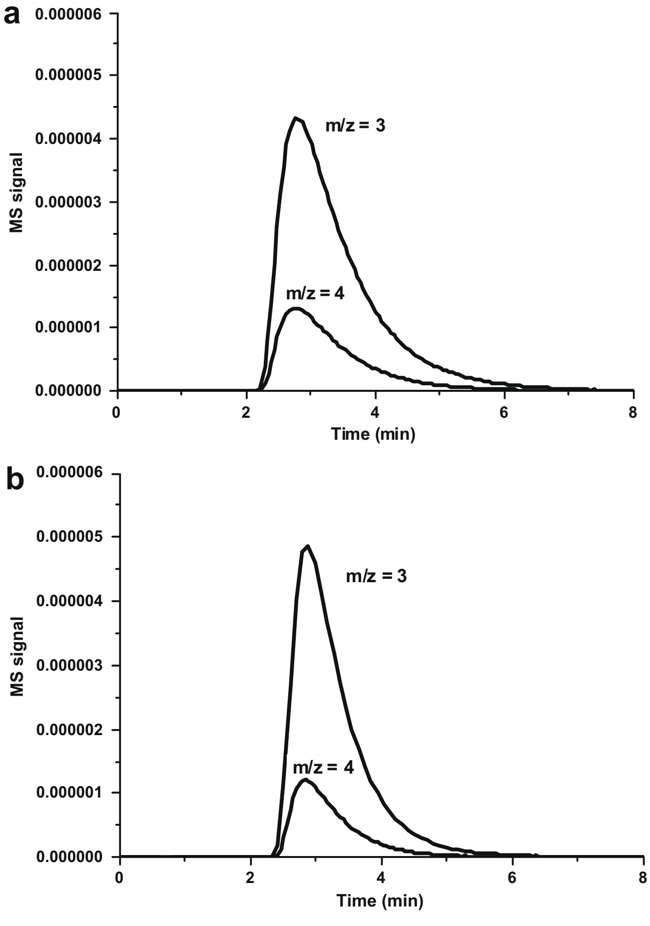


Fig. 3. H_2/D_2 exchange over (a) HZSM-5 and (b) 3Ga/HZSM-5 at 550 °C in the pulse mode.

Table 4
Activity of H_2/D_2 exchange of various catalysts.

Type of catalyst	Temperature (°C)	Area ratio of H–D/D–D
HZSM-5	450	3.18
	500	3.33
	550	3.44
3Ga/HZSM-5	450	3.52
	500	4.00
	550	4.22

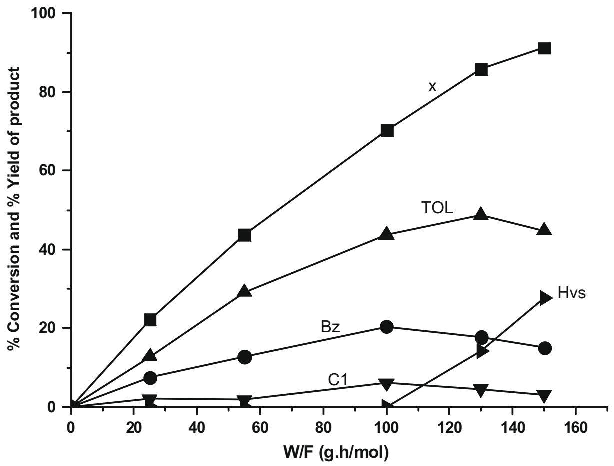


Fig. 4. Product distribution as a function of weight time (*W*/*F*). Total conversion (■); benzene (•); toluene (▲); methane (▼); and heavy oxygenates (►). *Reaction conditions:* catalyst = 3Ga/HZSM-5, *W*/*F* = 25–150 g h/mol, reaction temperature = 500 °C, carrier gas = H_2, and pressure = 1 atm.

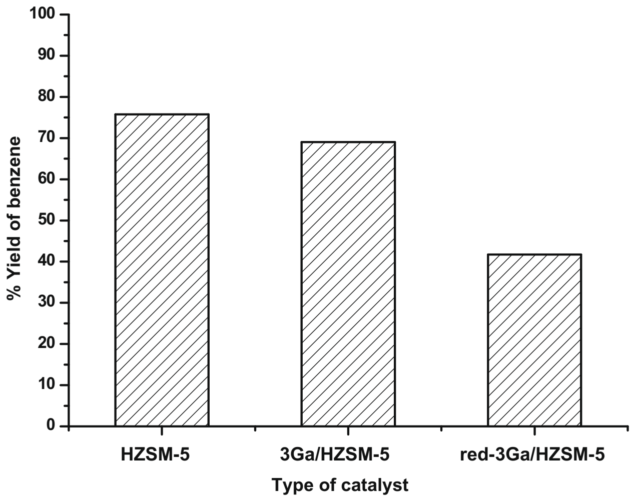


Fig. 5. Effect of catalyst pretreatment on the benzene yield. *Reaction conditions: W*/*F* = 100 g h/mol, reaction temperature 500 °C, carrier gas = He, pressure = 1 atm, and catalysts = HZSM-5, 3Ga/HZSM-5, and red-3Ga/HZSM-5 (reduced in H_2 at 550 °C for 2 h and then cooled down to 500 °C under He).

cies can be incorporated into the framework, possibly by the reaction with silanol defects. This incorporation would lead to additional Brønsted acid sites, as evidenced by solid state ^{1}H NMR and FTIR.

H_2/D_2 scrambling over HZSM-5 and 3Ga/HZSM-5 was monitored with an MS detector and the results are shown in Fig. 3 and Table 4. It is known that H_2/D_2 exchange to form H–D ($m/z = 3$) can be promoted over acid–base site pairs in oxides and zeolites [42]. Over HZSM-5, D_2 is thought to interact with an acidic proton and the counter framework oxygen forming an +H–D–D triad (three centers–two electrons) [43] that becomes the transition state for the H–D formation. As shown in Fig. 3, the 3Ga/HZSM-5 exhibited a higher H/D exchange activity than the HZSM-5 which as proposed before can be ascribed to the ability of Ga sites to act as "portholes" for hydrogen adsorption and desorption.

3.2. Catalytic activity in a continuous flow reactor

3.2.1. Product distribution

As seen in Fig. 4, over 3Ga/HZSM-5 benzaldehyde is converted mainly to benzene and toluene, which are the expected products from decarbonylation and hydrogenation/hydrogenolysis, respectively. The observed increase in benzene and toluene yields with *W*/*F* suggests that they are mostly formed as primary products, in parallel. The small amount of methane observed at high *W*/*F* may be the result of hydrodealkylation of toluene. Also, at high *W*/*F*, heavier secondary products such as xylenes and condensation oxygenated compounds are also observed. Xylenes are possibly derived from the toluene disproportionation, while the oxygenates can be generated from the secondary reaction of benzaldehyde with the decarbonylated/hydrogenolyzed species.

As shown in Table 5, in contrast to the Ga-containing catalysts, the parent HZSM-5 catalyst does not produce any toluene as a product. This remarkable difference suggests that the formation of toluene requires the hydrogenation/hydrogenolysis activity only provided by Ga. By contrast, the Brønsted acid sites may only be active for the decarbonylation to benzene. It is important to note that the NaZSM-5 zeolite did not show any activity under the same reaction conditions.

Another important result included in Table 5 is the effect of the carrier gas used in the reaction. That is, even on the Ga-containing catalysts, toluene was only formed in the presence of hydrogen. Benzaldehyde conversion over 3Ga/HZSM-5 using He as a carrier gas only yielded benzene as a product. On the HZSM-5 catalyst, the presence or absence of H_2 did not significantly affect the activity or product distribution indicating that decarbonylation does not require hydrogen to occur on the Brønsted acid sites. Previous studies have shown that HZSM-5 readily catalyzes the direct decarbonylation of aldehydes. For example, Grandmaison et al. [44] have reported that furfuraldehyde is converted over HZSM-5 to furan via direct decarbonylation on acid sites.

The role of Brønsted acid sites in the formation of benzene is further supported by the differences observed in benzene yield over the 3Ga/HZSM-5 catalyst after treatment in H_2 compared to the treatment in He. As shown in Fig. 5, the lower benzene yield obtained on the catalyst treated in H_2 correlates with the lower

Table 5
Effect of Ga and type of carrier gas.

Type of catalysts	Temperature (°C)	Carrier gas	% Conversion	Product distribution (% yield)		
				Benzene	Toluene	Methane
HZSM-5	450	He	56.32	56.32	0.00	0.00
		H_2	54.23	54.23	0.00	0.00
3Ga/HZSM-5	450	He	55.80	55.80	0.00	0.00
		H_2	58.20	19.95	36.40	1.85
3Ga/HZSM-5	500	He	69.07	69.07	0.00	0.00
		H_2	70.22	20.42	43.71	6.09

Reaction conditions: catalyst = HZSM-5, 3Ga/HZSM-5, *W*/*F* = 100 g h/mol, reaction temperature = 450 and 500 °C, carrier gas = He and H_2, and pressure = 1 atm.

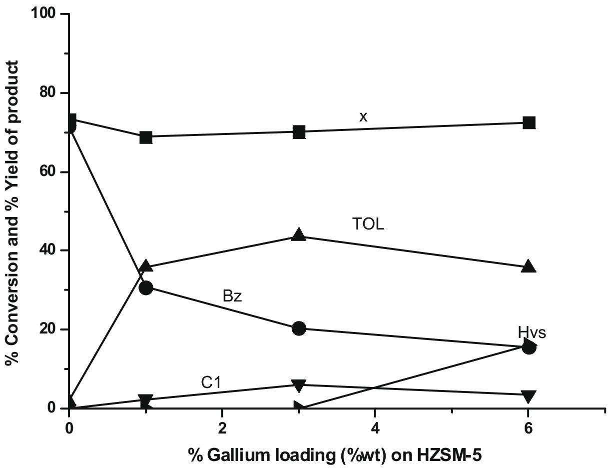


Fig. 6. Product distribution as a function of Ga loading. Total conversion (■); benzene (•); toluene (▲); methane (▼); and heavy oxygenates (▶). *Reaction conditions: W/F* = 100 g h/mol, reaction temperature = 500 °C, carrier gas = H_2, and pressure = 1 atm.

Table 6
Effect of support.

	Type of catalyst		
	$3Ga/SiO_2$	3Ga/HZSM-5	3Ga/HZSM-5
W/F (g h/mol)	100	100	20
Temperature (°C)	550	550	500
Conversion (%)	20.22	97.50	22.25
Yield (%)			
Methane	0.00	8.91	2.00
Benzene	6.10	24.21	7.46
Toluene	14.12	64.37	12.79
Selectivity (%)			
Methane	0.00	9.14	8.99
Benzene	30.17	24.83	33.53
Toluene	69.83	66.03	57.48

Reaction conditions: catalyst treated with H_2 at 550 °C for 2 h, reaction temperature = 550 °C, carrier gas = H_2, and pressure = 1 atm.

density of Brønsted acid sites remaining on this catalyst after the reduction treatment (see Table 3). As mentioned above, the reduction of Ga leads to the formation of Ga cationic species that can replace Brønsted acid sites, thus causing a decrease in decarbonylation activity.

Fig. 6 describes the effect of varying the Ga loading in the HZSM-5 zeolite. It is seen that the increase in Ga content enhances the selectivity toward toluene as opposed to benzene. This is due to the increase in hydrogenation/hydrogenolysis activity provided by the incorporated Ga species. At the highest Ga loading, a decrease in toluene yield along with an increase in high MW oxygenates can be observed. As toluene is the dominant primary product, it is possible that higher loading of Ga promotes the secondary reactions to form condensation products. When toluene was co-fed with benzaldehyde over Ga-modified HZSM-5 catalyst even higher yields of high MW oxygenates were obtained.

The effect of varying the reaction temperature is illustrated in Fig. 7a and b for the HZSM-5 and 3Ga/HZSM-5 catalysts, respectively. Over HZSM-5, benzene is the predominant product at all temperatures, only at the highest temperature investigated a small amount of toluene was produced, presumably associated with hydrogen transfer from carbonaceous deposits formed at the higher temperature.

To compare the activity of a Ga catalyst supported on a non-acidic support to those of the Ga-zeolites, the benzaldehyde reaction was carried out on the $3Ga/SiO_2$ catalyst. The comparison is made in Table 6 which shows that under the same reaction conditions as those used for the zeolites catalyst, the silica-supported Ga catalyst displays a significantly lower activity, that is, to reach the same low conversion as that of the silica-supported catalyst, the Ga-zeolite had to be run at a *W/F* five times lower. This low activity is certainly due to the much lower acidity of the silica support than the zeolite. In addition, silica may not stabilize the Ga species in as highly dispersed form as those obtained over the zeolites. This difference is further confirmed by the TPR results (see Fig. 1), which showed that much higher temperatures were needed to reduce the silica-supported gallium oxide species than those of comparable loading supported on the zeolites, and no reduction was observed at the low temperature region at which highly dispersed Ga species are expected to get reduced.

3.2.2. Effect of addition of water to the feed

Since water is always present in every biomass-conversion process, such as the fast pyrolysis that is the focus of our interest [45,46], we have studied the effect of adding water vapor to the benzaldehyde feed. The results are summarized in Table 7. As ex-

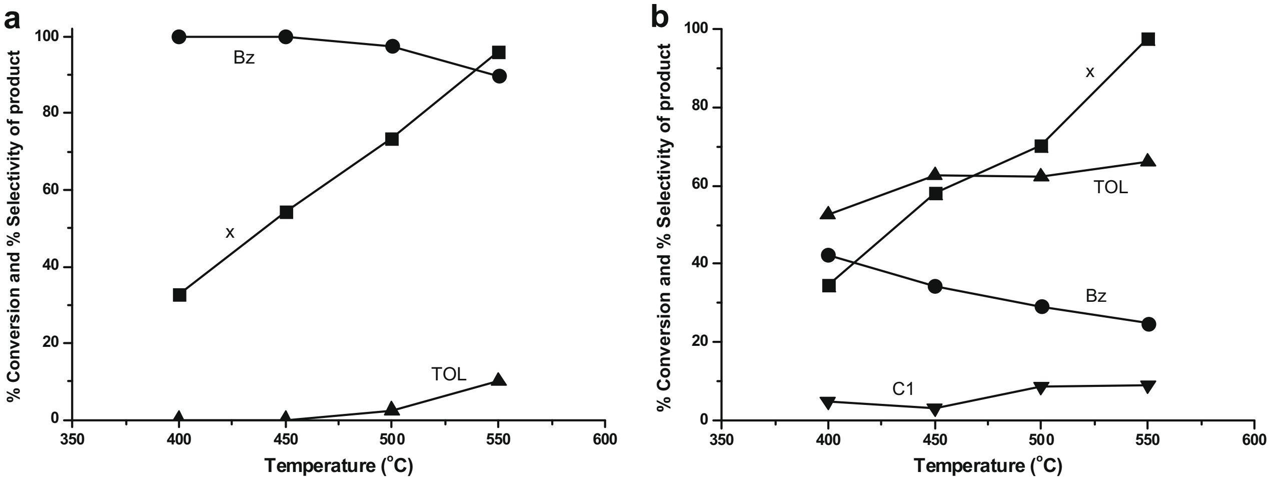


Fig. 7. Product distribution as a function of temperature over (a) HZSM-5 and (b) 3Ga/HZSM-5 Total conversion (■); benzene (•); and toluene (▲). *Reaction conditions:* catalyst = HZSM-5, 3Ga/HZSM-5, *W/F* = 100 g h/mol, reaction temperature = 400–550 °C, carrier gas = H_2, and pressure = 1 atm.

Table 7
Effect of water co-feeding.

Catalyst	Carrier gas	% Conversion	Product distribution (% yield)		
			Benzene	Toluene	Methane
HZSM-5	He	56.32	56.32	0.00	0.00
	He + water	51.14	51.14	0.00	0.00
3Ga/HZSM-5	He	55.80	55.80	0.00	0.00
	He + water	67.52	67.52	0.00	0.00
3Ga/HZSM-5	H_2	58.20	19.95	36.40	1.85
	H_2 + water	65.19	46.94	18.24	0.00

Reaction conditions: catalyst = HZSM-5, 3Ga/HZSM-5, *W*/*F* = 100 g h/mol, reaction temperature = 450, carrier gas = He and H_2, and pressure = 1 atm.

pected, the conversion of benzaldehyde to benzene over the unpromoted HZSM-5 slightly decreases with the presence of water in the feed, which one can explain by the competitive adsorption of water over the acid sites. Interestingly, in the case of 3Ga/HZSM-5 the benzene yield under He actually increased with the addition of water to the feed. This increase must be certainly due to the enhanced acid density seen in the IPA-TPD experiments (Fig. 2 and Table 3) when the 3Ga/HZSM-5 was treated with water vapor at 450 °C. When the activity comparison was made under H_2, it was also seen that the yield of benzene increased when water was present in the feed, but on the contrary, the toluene yield dropped considerably. This decrease in toluene yield suggests that water may alter the nature of the Ga species causing a decrease in their hydrogenation/hydrogenolysis activity. It is interesting to note in Fig. 8 that the presence of water causes the increase in the benzene/toluene ratio mentioned above, but this ratio can be decreased after water is withdrawn from the reaction stream suggesting that the effect of water is partially reversible. However, as shown in Fig. 8, when water is injected again in the feed, the enhancement in benzene formation is less pronounced, perhaps related to a decrease in the number of acid sites that can be regenerated.

3.3. Transient catalytic experiments

3.3.1. TPD of adsorbed benzaldehyde

To further investigate the different reaction paths that occur on these catalysts under different gases and pretreatments, we conducted TPD measurements of adsorbed benzaldehyde over the 3Ga/HZSM-5 sample treated and run in three different ways. (a) Treatment and TPD in He, (b) treatment in H_2, TPD in He, and (c) treatment and TPD in H_2.

In the three cases, the sample was treated (in He or H_2) at 550 °C for 2 h. Benzaldehyde was added in pulses at 180 °C until saturation, the sample was flushed with He (or H_2), and the heating ramp was started using He (or H_2) as the carrier gas. Fig. 9 shows the evolution of the products evolved from the catalyst during the heating process. In the He/He case, no toluene was observed, but mostly benzene and CO, the two products expected from the decarbonylation reaction, were observed. At the very high-temperature range, further evolution of CO and water was observed, which can be ascribed to the decomposition of some oxygenated fragments that may remain on the surface. In the H_2/He case, there is lower production of benzene and CO, which is in agreement with the reduction of the density of acid sites, as explained above. More interestingly, toluene is observed in this transient experiment, a product that was not observed in the flow experiments in the absence of hydrogen. In fact, the hydrogenation/hydrogenolysis reactions require H_2 for production of toluene in steady state. However, one can expect that if the surface retains hydrogen it will be able to produce toluene in a transient experiment, as observed. Therefore, we can conclude that the reduced Ga species can be responsible for retaining chemisorbed hydrogen, presumably in the form of GaH_2^+, as suggested by Kazansky et al. [32], who indicate that GaH_2^+ species are relatively stable and decompose in the absence of H_2. Finally, in the H_2/H_2 case, the major product is toluene, as expected, with a much lower production of benzene and CO.

3.3.2. Benzaldehyde pulse reaction

In the pulse mode, the benzaldehyde is injected over a clean catalyst sample in the atmosphere given by the carrier gas, He or H_2. As shown in Fig. 10 and in good agreement with the results obtained in the flow mode or with TPD of adsorbed benzaldehyde, the

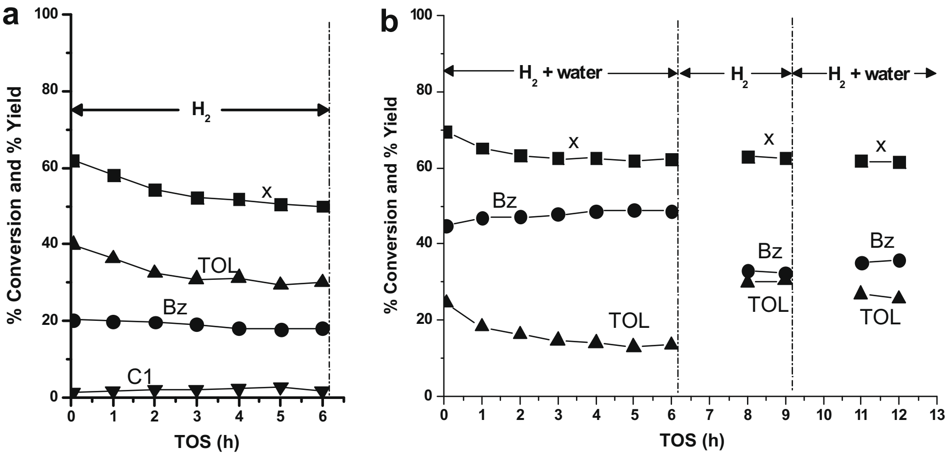


Fig. 8. Effect of co-feeding water (a) reaction without water; and (b) reaction with water (6 h), then removed (3 h), and then injected again. *Reaction conditions:* catalyst = 3Ga/HZSM-5, *W*/*F* = 100 g h/mol, reaction temperature 450 °C, carrier gas = H_2, and pressure = 1 atm.

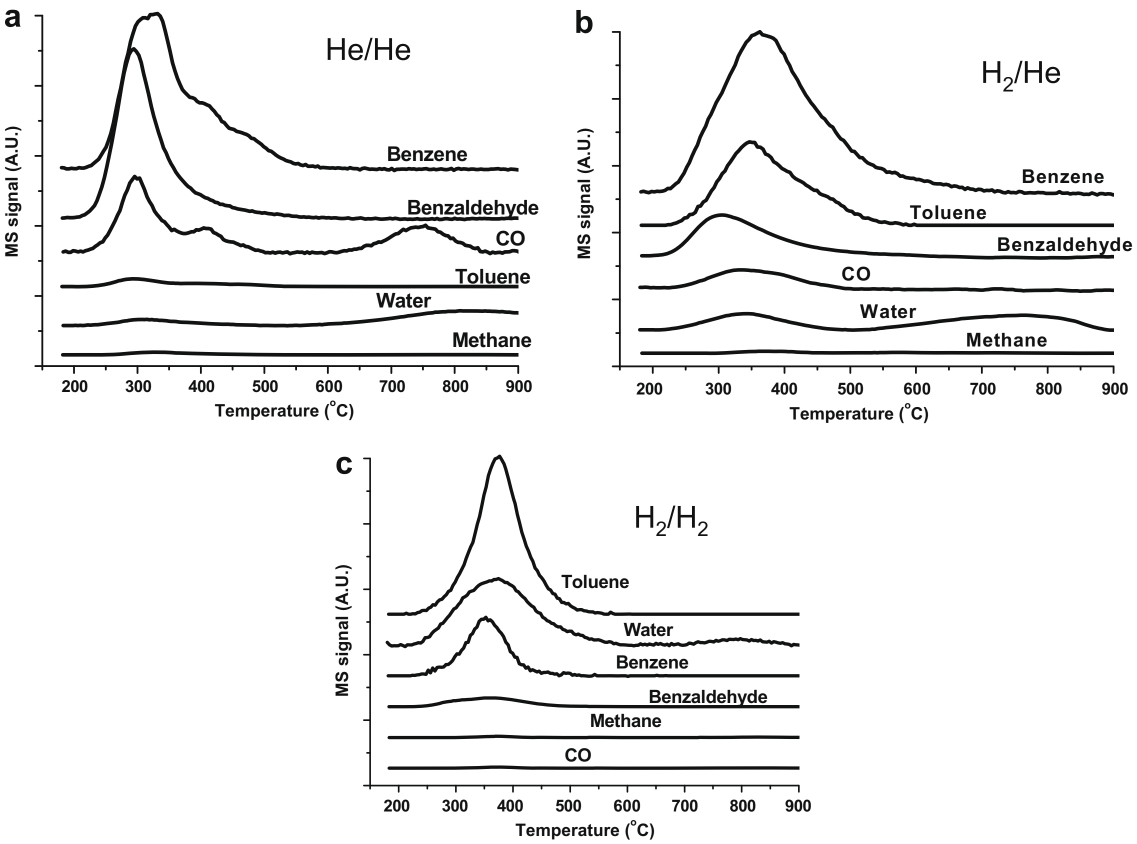


Fig. 9. Product evolution during benzaldehyde – TPD over a 3Ga/HZSM-5 catalyst treated and run as follows: (He/He) pretreated in He at 500 °C and TPD run under He; (H_2/He) pretreated in H_2 at 500 °C and TPD run under He; and (H_2/H_2) pretreated in H_2 at 500 °C and TPD run under H_2.

dominant product under He is benzene, but under H_2 is toluene. The evolution of benzene is paralleled by comparable evolution of CO indicating that under He direct decarbonylation occurs. Likewise, the evolution of toluene under H_2 is paralleled by evolution of water. Under H_2, the production of benzene is significant and arises from two reaction paths, one is the direct decarbonylation that still occurs under H_2, and the second is the dealkylation of toluene, which is accompanied by evolution of methane. The relatively small amount of methane produced in the pulse compared to the amount of benzene shows that the contribution of this secondary reaction to the formation of benzene is significantly lower than that of the direct decarbonylation.

4. Discussion

Depending on the Ga loading in the catalyst and the operating conditions, benzaldehyde can undergo either decarbonylation or hydrogenation/hydrogenolysis yielding benzene or toluene as major product. When the HZSM-5 catalyst is promoted with Ga in a high state of dispersion, the benzaldehyde conversion under H_2 gas produces mainly toluene, as typically observed over metal-modified acid zeolites [47,48]. At higher *W*/*F* and higher reaction temperatures methane is observed in relatively low concentrations, as a secondary product, most probably derived from the hydrodealkylation of toluene. Also, at high *W*/*F* and high Ga loadings small amounts of xylenes and heavier oxygenated compounds are obtained. They are secondary products of toluene disproportionation and condensation reactions that occur at high toluene concentrations.

It is proposed that the hydrogenation/hydrogenolysis activity is due to the presence of reduced Ga species (i.e. Ga^+/GaH_2^+) generated over the zeolites after heating in H_2. The TPR and IPA-TPD results (see Figs. 1 and 2) provide some insight into the chemistry responsible for the formation of these reduced Ga species. Reduction of octahedrally coordinated Ga^{3+} ions in Ga_2O_3 clusters leads to the formation of reduced univalent Ga^+ ions, which can replace Brønsted acid sites in the zeolites [22,30,49,50], according to the following

$$Ga_2O_3 + 2H_2 \rightarrow Ga_2O + 2H_2O \tag{1}$$

$$Ga_2O + 2H^+Z^- \rightarrow 2Ga^+Z^- + H_2O \tag{2}$$

where Z^- represents the negative framework charge of zeolite.

Evidence in favor for this reduction and acid site replacement processes come from the observed H_2 consumption (Table 2) and the parallel decrease in Brønsted acid site (Table 3), respectively, when the Ga/HZSM-5 catalyst was reduced in H_2.

The transient experiments indicate that, after the formation of Ga^+ by H_2 reduction, the Ga^+ ions can further chemisorb hydrogen, resulting in the formation of gallium dihydrides (GaH_2^+), as previously proposed [36,49,51,52], according to the expression

$$Ga^+Z^- + H_2 \rightarrow GaH_2^+Z^- \tag{3}$$

The existence of GaH_2^+ species has been spectroscopically demonstrated by Kazansky et al. [32]. Since hydride transfer plays an important role in the formation of toluene, it is believed that H_2 can not only keep Ga species in its reduced forms but also maintain GaH_2^+ species under steady-state reaction. These species can readily hydrogenate the carbonyl group of benzaldehyde forming benzyl alcohol, which then hydrogenolyze to form toluene and water. The formation of water, together with toluene, was evidenced by

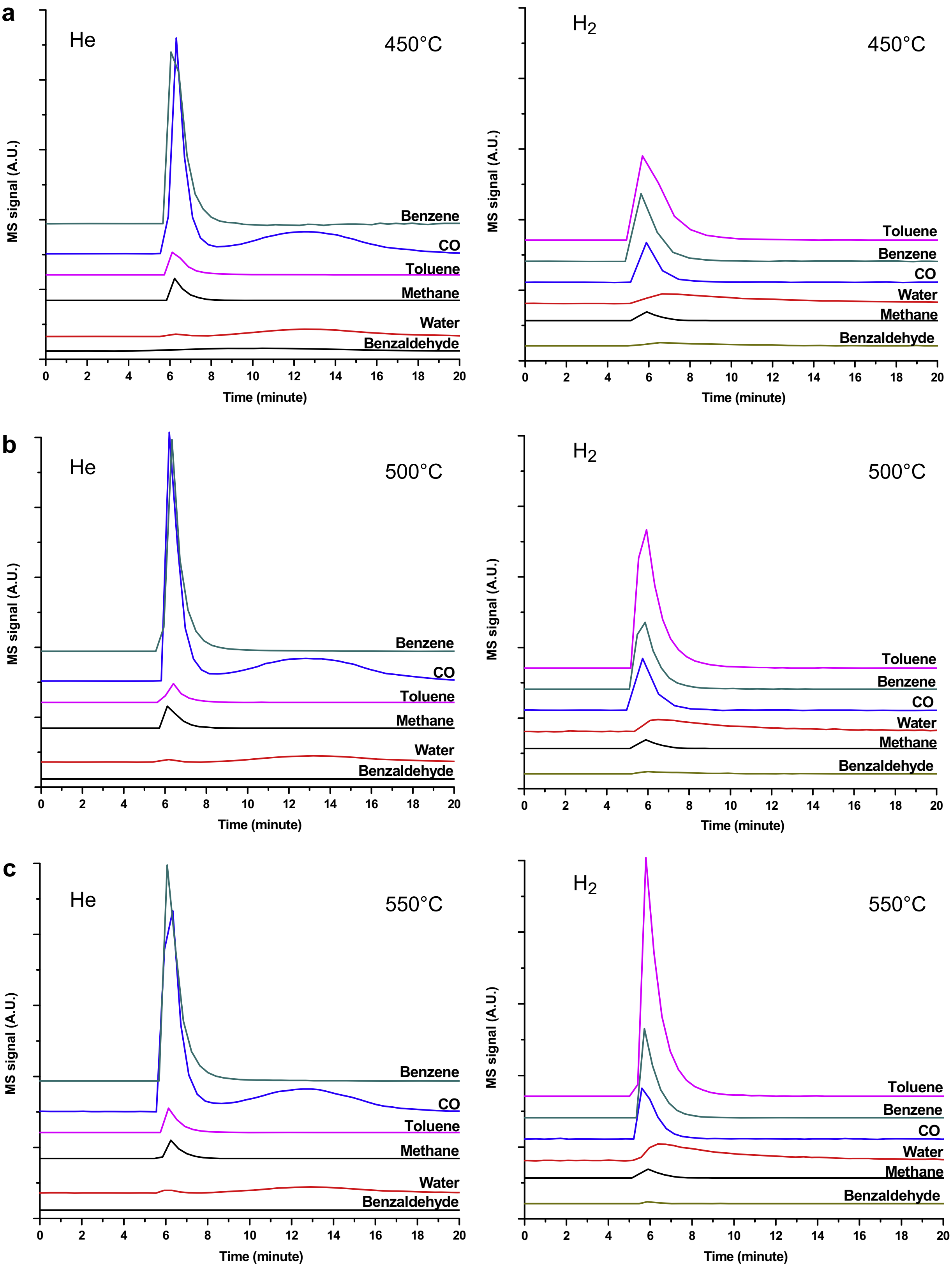


Fig. 10. Product distribution from the benzaldehyde conversion over 3Ga/HZSM-5 in pulse mode using He or H_2 as a carrier gas, and at temperatures of (a) 450, (b) 500, and (c) 550 °C.

the TPD experiments (see Fig. 9c), as well as by the benzaldehyde pulse reaction experiments (see Fig. 10).

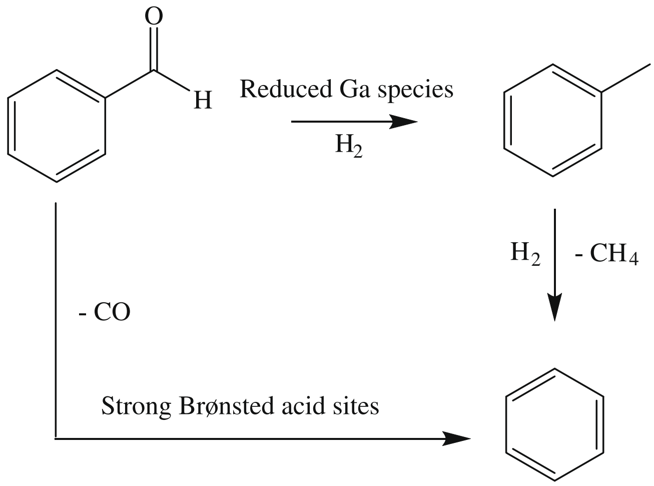
The GaH_2^+ species generated by the interaction of reduced Ga^+ species with H_2 (Eq. (3)) is possibly the active species for the enhanced H_2/D_2 exchange observed on the Ga-modified ZSM-5, relative to the HZSM-5. This process would involve the formation of a stable intermediate $(D)(Ga(H_2)(D))^+Z^-$ proposed by Gonzales et al. [43] as

$$\mathrm{Ga(H_2)^+Z^- + D_2 \rightleftarrows (D)(Ga(H_2)(D))^+Z^-} \tag{4}$$

$$\mathrm{(D)(Ga(H_2)(D))^+Z^- \rightarrow Ga(HD)^+Z^- + HD} \tag{5}$$

The D_2 molecule can dissociate into two D atoms; one interacts with the $Z^-GaH_2^+$ site, the other is bonded to an O atom in the zeolite framework. In the case of benzaldehyde conversion in the presence of gas-phase H_2, the GaH_2^+ species can possibly transfer the dissociated H_2 to the benzaldehyde and consecutively hydrogenolyze it forming toluene.

Benzene is formed primarily by benzaldehyde decarbonylation over the Brønsted acid sites. It can also be produced via toluene hydrodealkylation, with the formation of methane in parallel. The main reaction paths occurring on the catalysts investigated can be summarized in the following scheme.



Over non-reduced 3Ga/HZSM-5 catalyst and in the absence of H_2, only benzene is obtained. The addition of Ga does not seem to have any effect on this reaction, other than reducing the density of strong acid sites. In fact, the rate of benzene formation correlates very well with the number of strong acid sites. As shown in Fig. 11, when the rate of benzene formation is plotted as a function of the density of strong Brønsted acid sites, as measured by IPA-TPD (Table 3), a straight line results, which supports the concept that the direct decarbonylation of benzaldehyde to form benzene is catalyzed by strong Brønsted site.

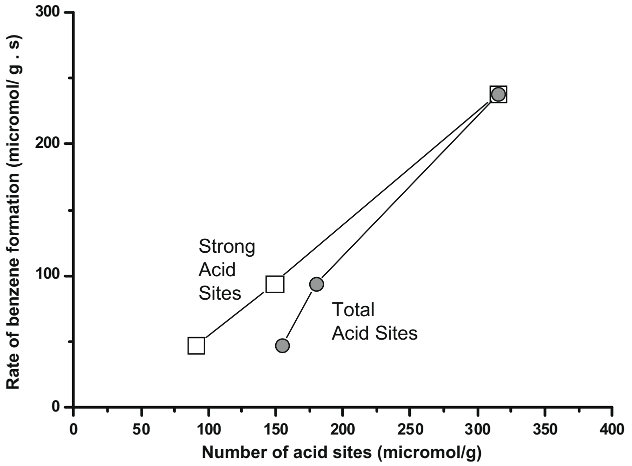


Fig. 11. Rate of benzene formation versus number of acid sites. *Reaction conditions*: catalyst = HZSM-5, 1Ga/HZSM-5, 3Ga/HZSM-5, W/F = 100 g h/mol, reaction temperature 500 °C, carrier gas = H_2, and pressure = 1 atm.

An interesting difference in the response to addition of water to the feed was observed between the unpromoted and the Ga-promoted HZSM-5. While the activity of the former decreased with water added to the feed, the activity of the latter increased. As mentioned above, the decrease in activity is simply due to the adsorption competition, while the increase parallels the increase in the density of Brønsted acid sites observed by IPA-TPD (Table 3). This increase can be interpreted in terms of the formation of GaO(OH) species according to the following steps, previously proposed [53–55]

$$\mathrm{Ga^+ + H_2O \rightarrow GaO^+ + H_2} \tag{6}$$

$$\mathrm{GaO^+ + H_2O \rightarrow GaO(OH) + H^+} \tag{7}$$

Some of us [41] have recently proposed that the GaO(OH) species can be incorporated into the zeolites framework by reaction with available silanol defects, forming additional Brønsted acid sites (≡Ga–OH–Si≡), according to

$$\mathrm{GaO(OH) + 4(\equiv Si{-}OH) \rightarrow GaH(OSi\equiv)_4 + 2H_2O} \tag{8}$$

Under H_2, the dominant hydrogenation/hydrogenolysis activity of Ga/HZSM-5 decreased while decarbonylation increased when water was added. Based on the concepts discussed above, the interaction of water with the Ga cationic species not only forms additional Brønsted sites, which accounts for the enhanced decarbonylation, but also reduces the number of GaH_2^+ species, active for hydrogenation/hydrogenolysis. Interestingly, the hydrogenation/hydrogenolysis activity can be recovered when water is removed from the feed, which indicates that Eqs. (7) and (6) are reversible.

5. Conclusions

The benzaldehyde conversion over Ga/HZSM-5 yields benzene and toluene as main products. Benzene is produced mainly by direct decarbonylation over Brønsted acid sites. Toluene is only produced in the presence of H_2 by hydrogenation/hydrogenolysis over GaH_2^+ species. These species are only generated under H_2. No toluene is formed in steady state in the absence of H_2. The presence of water causes an increase in the benzene/toluene ratio in the products from Ga-modified HZSM-5.

Acknowledgments

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