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Effect of reductive and oxidative atmospheres on the propane aromatisation activity and selectivity of Ga/H-ZSM-5 catalysts

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Abstract

The aromatisation of propane was investigated at 823 K on two Ga/H-ZSM-5 catalysts differing by their aluminum content (Si/Al = 18 and 128, respectively), i.e. their Brönsted acid site concentration, and having similar gallium content (1.6 wt%) as a function of successive pretreatments by hydrogen and oxygen. Hydrogen treatment increases activity and selectivity to aromatics while decreasing the formation of methane. Subsequent oxygen treatment enhances further the activity and aromatics selectivity and has little effect on methane selectivity. These improvements of catalytic performance are explained by gallium migration in reducing conditions. The concentration of highly dispersed gallium species is thereby enhanced. These species, in association with Brønsted centers, were reported previously to constitute the dual catalytic sites responsible for alkane activation. Hydrogen–oxygen pretreatment of Ga/H-ZSM-5 catalysts is thus a means to ensure rapid catalyst preactivation and stabilisation in large scale light alkane aromatisation units.

Keywords: Reductive atmospheres; Oxidative atmospheres; Propane aromatisation; Activity and selectivity; Ga/H-ZSM-5 catalysts

1. Introduction

Ga/H-ZSM-5 catalysts are most active and selective for the aromatisation of propane [1]. It is widely accepted that their activity and selectivity result from their bifunctional properties, whereby gallium species are responsible for their dehydrogenation–hydrogenation activity and the Brönsted acid sites of the zeolite provide the centres necessary for chain growth.

Recently, it was shown that dual active sites are responsible for the activation of propane on Ga/H-ZSM-5 [2–4]. These dual active sites consist of highly dispersed (Ga^{3+}, O^{2-}) ions pairs, acting in synergy with neighbouring Brönsted sites which initially activate propane as a protonated pseudo-cyclopropane species.

Changes in the propane aromatisation activity and selectivity of these catalysts as a function of the number of reaction (reducing conditions)–regeneration (oxidative conditions) cycles sustained were explained by the migration of gallium species in and out of the zeolite intracrystalline void space [5] as substantiated by detailed catalyst characterisation [6].

Several authors, including us, proposed that gallium is reduced under reaction conditions and that its migration involves Ga(I) species

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Table 1
Distribution of some aluminium and gallium species in catalysts Z234 and Z356 [2,6] [a]

	Al_T / uc	Ac sites/ uc	Ga_T / uc	Ga_{ionex} / uc	Ga_{ND} / uc
1. Z234 SL2	3.70	2.60	0.22	0.92	0.18
2. Z356 SL1	1.14	0.99	0.15	0.25	0.92
Ratio 1/2	3.24	2.60	1.47	3.68	0.20

[a] Al_T /uc, number of tetrahedral Al sites per unit cell; Ac sites/uc, number of acidic sites per unit cell; Ga_T /uc, number of tetrahedral Ga sites per unit cell; Ga_{ionex} /uc, number of ion-exchanged Ga species per unit cell; Ga_{HD} /uc, number of highly dispersed Ga species per unit cell.

[1,2,7–18]. Migration of Ga_2O species via the vapour phase was postulated by us but solid state ion-exchange [19] was not ruled out as another possibility [1,2,5,6]. A debate was also initiated recently about the possible and reversible formation of a catalytically active site at the interface between Ga_2O_3 and zeolite H-ZSM-5, with no induction period, when a mechanical mixture of these two solids is exposed to reaction conditions [20–23]. The appearance of such new active sites could be related to the rapid reduction of some Ga(III) by hydrogen released as aromatisation is initiated.

Several authors have also reported the inhibitory effect of hydrogen on propane transformation over Zn/H-ZSM-5 [24] and Ga/H-ZSM-5 catalysts [25]. A possible explanation is that the limiting step of the propane dehydrogenation is the removal of hydrogen [26]. Another is that competitive adsorption of hydrogen inhibits the formation of the protonated pseudo-cyclopropane intermediate responsible for the initial activation of propane [1,2].

The present contribution aims at clarifying the role of reductive (hydrogen) and oxidative (oxygen) atmospheres in the activation of Ga/H-ZSM-5 catalysts for propane aromatisation.

2. Experimental

2.1. Catalysts preparation and characterisation

The preparation, activation, and characterisation of the two Ga/H-ZSM-5 catalysts used in the present study have been described previously [2,3,6].

Chemical and physical distributions of Al and Ga species were derived as described elsewhere [2,6] by combining solid state ^{71}Ga, ^{27}Al and ^{29}Si MAS NMR results with NH_3-TPD data for the fresh and used catalysts exchanged with ammonium ions at pH = 9, in order to measure

Table 2
Effect of H_2–O_2 treatment cycles on propane conversion and product selectivities (wt% C) in propane aromatisation reaction on Z234 SL2 catalyst

Treatment	Conversion (wt.%)	Product selectivities (wt% C)						
		C_1	C_2	$C_{2=}$	$C_{3=}$	C_4^+	$C_{4=}$	Aromatic
Initial	5.3	10.0	2.8	17.9	40.3	5.0	5.1	18.9
H_2-1st	6.0	8.1	4.6	15.7	39.2	4.8	5.0	22.5
O_2-1st	7.9	7.7	4.7	12.9	32.2	5.2	4.1	32.8
H_2-2nd	8.1	7.6	5.5	12.8	31.7	5.8	4.4	32.2
O_2-2nd	8.7	7.8	4.7	12.3	30.2	5.8	3.9	35.2
H_2-3rd	8.9	7.6	5.4	12.3	29.7	5.9	4.0	35.0
O_2-3rd	7.9	9.0	4.2	13.2	30.2	6.2	3.7	33.5
H_2-4th	8.1	8.2	4.7	12.7	31.1	6.0	3.7	33.5
O_2-4th	7.8	8.8	4.4	12.7	30.1	6.1	3.9	34.0
H_2-5th	8.1	8.1	4.8	12.8	31.2	6.0	3.9	33.3
O_2-5th	8.1	8.3	4.4	13.0	30.9	6.1	3.8	33.4
H_2-6th	7.8	8.2	4.8	12.4	30.3	5.8	4.0	34.5
O_2-6th	8.0	8.8	4.1	13.5	31.5	6.2	3.9	31.9

Table 3
Effect of H_2–O_2 treatment cycles on propane conversion and product selectivities (wt% C) in propane aromatisation reaction on Z356 SL1 catalyst

Treatment	Conversion (wt%)	Product selectivities (wt% C)						
		C_1	C_2	$C_{2=}$	$C_{3=}$	C_4^+	$C_{4=}$	Aromatic
Initial	0.99	22.2	1.2	33.2	43.1	0	0	0.3
H_2-1st	2.88	8.2	4.1	14.6	51.8	2.5	0	16.0
O_2-1st	5.10	8.4	3.9	14.1	37.6	3.7	3.2	29.0
H_2-2nd	4.50	7.5	4.7	13.3	41.9	3.5	3.3	25.8
O_2-2nd	5.70	8.0	3.9	13.9	37.1	3.7	3.3	30.1
H_2-3rd	5.20	7.5	4.6	13.6	39.3	3.4	3.4	28.2
O_2-3rd	5.60	8.5	3.4	14.3	36.5	3.8	3.5	29.9
H_2-4th	5.00	7.4	4.3	13.9	40.3	3.4	3.5	27.1
O_2-4th	5.60	7.9	3.8	13.7	36.9	3.6	3.4	30.5
H_2-5th	5.00	7.3	4.7	13.6	40.9	3.3	3.7	26.5
O_2-5th	5.80	7.7	3.9	13.8	36.9	3.6	3.3	34.3
H_2-6th	5.20	7.1	4.4	13.8	40.4	3.3	3.6	27.2
O_2-6th	5.50	8.2	3.5	14.6	37.7	3.8	3.5	28.7

quantitatively all Brönsted acid sites associated to the aluminium species in the zeolite framework [27].

Table 1 summarises the main characteristics of the two catalysts.

2.2. Catalyst testing

Catalytic performances were evaluated at 823 K ($P = 1$ bar; pure feed $= C_3H_8$). Catalytic testing and product analyses were performed as described earlier [2,5,6]. Hydrogen–oxygen pretreatments were performed at 823 K (1 h in H_2 and 1 h in O_2, $P = 1$ atm, 2.0 l h^{-1}). Activity and selectivity for the conversion of propane following H_2–O_2 pretreatments were measured after 2 min time-on-stream at 823 K.

3. Results and discussion

The catalytic performances of both catalysts exposed from none to six H_2–O_2 cycles are shown in Tables 2–4 and Fig. 1.

Table 4
Effect of H_2–O_2 treatment cycles to the balance in cracking and dehydrogenating functions

Sample	Treatment	Product selectivities (wt% C)			Molar ratios in products	
		C_1	$C_{3=}$	Aromatic	$C_{2=}/C_2$	H/C
Z234 SL2	Initial	10.0	40.3	18.9	6.4	2.06
	H_2-1st	8.1	39.2	22.5	3.4	2.00
	O_2-1st	7.7	32.2	32.8	2.7	1.89
	H_2-2nd	7.6	31.7	32.2	2.3	1.91
	O_2-2nd	7.8	30.2	35.2	2.6	1.88
	H_2-3rd	7.6	29.7	35.0	2.6	1.88
	O_2-3rd	9.0	30.2	33.5	3.1	1.92
Z356 SL1	Initial	22.2	43.1	0.3	2.7	2.45
	H_2-1st	8.2	51.8	16.0	3.6	2.00
	O_2-1st	8.4	37.6	29.0	3.6	1.93
	H_2-2nd	7.5	41.9	25.8	2.8	1.96
	O_2-2nd	8.0	37.1	30.1	3.6	1.92
	H_2-3rd	7.5	39.3	28.2	3.0	1.93
	O_2-3rd	8.5	36.5	29.9	4.2	1.92

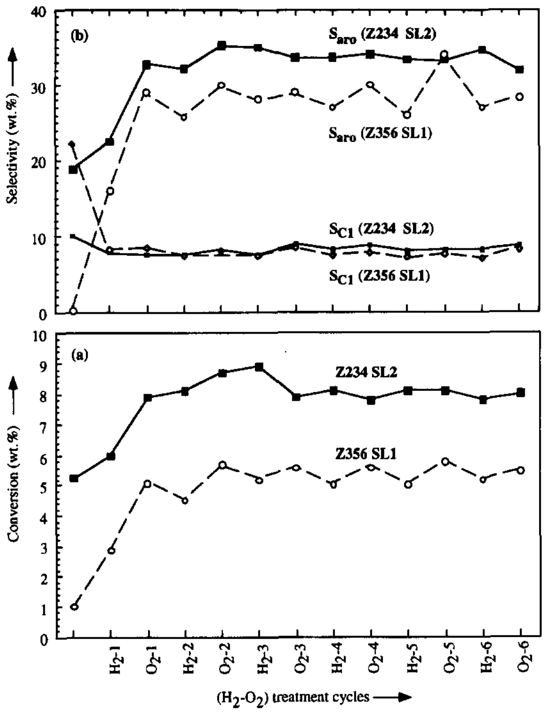


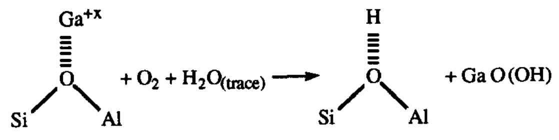
Fig. 1. Effect of H_2–O_2 treatment cycles on (a) the conversion of propane and (b) the product selectivities in the aromatisation reaction ($T = 823$ K, $P = 1$ bar, propane flow rate = 2.0 l h^{-1}) using Z234 SL2 (catalyst weight = 12.4 mg) and Z356 SL1 (catalyst weight = 26.0 mg) catalysts.

The conversion of propane and the aromatisation selectivity increase significantly when the catalysts are exposed to H_2 pretreatment: after the first H_2 exposure, activity increases by 15% for Z234 SL2 and 200% for Z356 SL1. The first O_2 treatment also increases catalyst activity and aromatisation selectivity: activity increases by 30% for Z234 SL2 and 100% for Z356 SL1. Interestingly, the selectivity to methane is decreased by the first H_2 treatment but not by the first O_2 treatment whereas both the first H_2 and O_2 treatments increase aromatisation selectivity. Subsequent H_2 and O_2 treatments have only a marginal effect on catalyst activity and selectivity.

These observations are consistent with the previously observed migration of gallium species under reducing atmosphere. Thermodynamics indicates that in the presence of hydrogen ($P = 1$ bar) at 823 K, Ga_2O_3 is reduced to Ga_2O with an equilibrium vapour pressure of Ga_2O equal to 2.38×10^{-8} bar [2,3] and several data confirm that the gallium deposited/ion-exchanged on the zeolite catalysts reduces from Ga(III) to Ga(I) [2,6–8]. The vapour phase Ga_2O species are highly mobile [2,3,5,10] but migration of Ga(I) species through the vapour phase does not exclude the migration/dispersion via other mechanisms such as solid-state ion-exchange [19]. Ga_2O species may be converted to Ga^+ ions by reaction with the Brönsted acid sites of the zeolite, leading to highly dispersed gallium species that are further oxidised by treatment in oxygen to yield highly dispersed Ga^{3+} entities.

These physical and chemical transformations of gallium species are responsible for the activity–selectivity changes in the initial reaction–regeneration cycles of propane aromatisation at 823 K [2,3,5,6] and agree with the proposals of several authors [10,11,13,14]. In particular, Meriaudeau et al. [28,29] showed that the Brönsted sites concentration was reduced and that Lewis acid sites were generated after hydrogen treatments, which is consistent with the probable ion-exchange of Brönsted sites by Ga ions and the Lewis acid site nature of highly dispersed Ga^{3+} species. In agreement with Meriaudeau, we also reported earlier that Z234 SL2, after three reaction–regeneration cycles, had lost part of its potential Brönsted acidity and contained more Lewis acid species [6].

The effect of H_2 exposure is summarised hereabove. The subsequent effect of oxygen has received less attention in the past. One possibility is illustrated below:



where traces of water may come from various sources including dehydroxylation, traces of water in the oxygen feed and the oxidation of

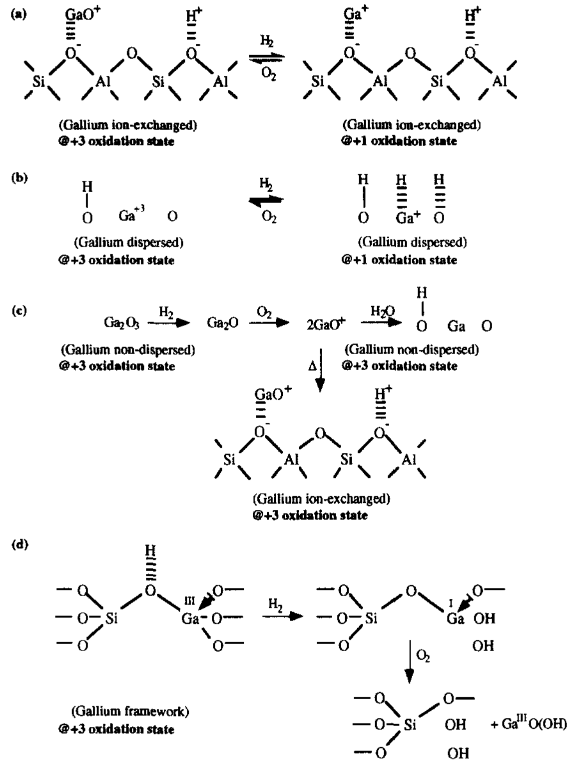


Fig. 2. Schematic representation of gallium species transformation under reducing and oxidising conditions.

carbonaceous residues when applied to a coked catalyst. This process increases the catalysts acidity in addition to dispersing the gallium modifier and could explain the further increase of activity and selectivity to aromatics when O_2 treatment follows H_2 treatment. Other possible transformations of the various gallium species in the presence of O_2 and traces of water are schematised in Fig. 2.

Thus, two major modifications may occur during O_2 treatment, which can increase activity and aromatics selectivity:

- The oxidation state of gallium species is restored to 3 + .
- The presence or the production (by coke burning) of steam causes partial degalliation of the framework and increase the concentration of dispersed gallium species.

Subsequent H_2–O_2 treatments do not cause any major increase in activity or variation in methane and aromatics selectivities. Thus, the role of such treatments after the first cycle would only be to maintain the dispersion, chemical state, and number of dispersed Ga_D species inside the zeolite.

As seen from Fig. 1 and Tables 2 and 3, the improvement in activity is much more drastic for Z356 SL1 than for Z234 SL2 after the first H_2–O_2 treatment. Z356 SL1 is the catalyst which has initially the lowest Ga dispersion, probably because of its lower Al content [2,3,6]. The enhancement in catalytic performance is mostly due to Ga redispersion as evidenced by RBS data. For both catalysts, subsequent H_2–O_2 treatments lead to oscillations of activity at almost constant level, sligthly higher after O_2 treatment than after H_2 treatment. The latter observation is tentatively explained by considering that Ga(III) is more efficient than Ga(I) to activate C_3H_8 by heterolytic abstraction of H_2 species as (a) it is more easily reduced to a lower oxidation state, and (b) as it is a stronger Lewis acid than Ga(I).

Table 4 shows the effect of H_2–O_2 pretreatments on the balance between the cracking and dehydrogenating functions, illustrated by the selectivities to methane, propene, and aromatics and the $C_{2=}/C_2$ and H/C ratio of the products.

The high initial CH_4 selectivity decreases upon successive treatments with hydrogen and oxygen. It is higher for catalyst Z356 SL1, in which about 70% of the gallium is initially non-dispersed and agglomerated at the external surface of the zeolite crystallites (compared to only 14% for Z234 SL2) [6], although Z356 SL1, contains about 2.6 times less acidic sites than Z234 SL2 (Table 1). Reoxidation of the catalysts by oxygen, following the hydrogen treatment, increases only slightly the CH_4 selectivity as shown over several successive H_2–O_2 cycles. Both catalysts have nearly the same methane selectivity after the first H_2–O_2 treatment.

Three factors may increase the selectivity to methane:

- Increasing acidity which favours cracking.

- Higher aromatics yield which leads to higher hydrogen production. The latter can released as methane and ethane (via acid-catalysed hydrogen transfer processes), or as molecular hydrogen on Ga species acting as portholes [17,18,26].
- The absence of an efficient route for the release of molecular hydrogen, namely if Ga species do not act efficiently as portholes to recombine hydrogen adatoms [17,18,26], i.e. as entities enabling the reverse spillover of hydrogen [31–33].

The data shown in Tables 2 and 3 show clearly that exposure to O_2 following the first H_2 treatment does not increase the methane and ethane selectivities although a significant increase in aromatics selectivity is observed. Hydrogen released by this higher aromatics selectivity is thus not transferred to C_1 and C_2 products which have a higher H/C ratio than propane. This point is confirmed by the average lower H/C ratio of the whole hydrocarbon products. Hence, desorption of dihydrogen must have been enhanced. We conclude that the dispersion of gallium resulting from the initial H_2–O_2 cycle generates Ga species which provide a porthole for efficient H_2 release via reverse hydrogen spillover as mentioned hereabove. We also conclude that the most active Ga species are in the oxidation state 3 + and that dehydrogenation processes and H-adatom recombination most probably involves the Ga(III)/Ga(I) redox couple. The latter supports earlier observations and proposals by other authors.

The $C_{2=}/C_2$ ratio varies in the same way as the change in CH_4 selectivity. A variation of the $C_{2=}/C_2$ ratio results from the combination of two factors: a decrease (or increase) of the selectivity to ethene and the opposite increase (or decrease) of the selectivity to ethane. It has been proposed that the $C_{2=}/C_2$ ratio measures the catalyst ability to transfer hydrogen [30].

The decrease of the $C_{2=}/C_2$ ratio for the Z234 SL2 catalyst could indicate a more efficient hydrogen transfer reaction in the presence of dispersed Ga species providing a dehydrogenation–hydrogenation function, where part of the ethene formed is being converted to ethane. However, it was observed that the decrease in ethene selectivity is very much in excess when compared to the increase in ethane selectivity (Table 2). Hence, the $C_{2=}/C_2$ ratio must be influenced by an additional (acid-catalysed) reaction pathway that consumes ethene, such as the formation of aromatics by conjunct polymerisation of ethene with other olefins. This proposal is supported by the fact that the increase in aromatics selectivity is almost quantitatively the sum of the decrease in ethene, propene, and butene selectivities and by the small variation of the $C_{2=}/C_2$ ratio for the Z356 SL1 catalyst which has a much lower concentration of acid sites.

The aromatisation selectivity, in both cases, increases during the first H_2–O_2 cycle to a relatively constant value of ca. 30% (slightly higher for Z234 SL2 compared to Z356 SL1). As expected, a higher selectivity to propene is observed for Z356 SL1 which is less acidic.

The average H/C ratio of the products decreases with increasing number of H_2 and O_2 cycles. Values are lower for Z234 SL2 compared to Z356 SL1, indicating the higher dehydrogenation and aromatisation activity of the former.

The evolution of the aromatisation selectivity and average H/C ratio are consistent with the view that (i) dispersed gallium species (more abundant in Z234 SL2) combined with Brönsted sites favour propane activation and aromatisation whereas non-dispersed Ga species, e.g. Ga_2O_3, at the outer surface of the crystallites is mostly a dehydrogenation component, and (ii) the need for carbon chain growth via acid-catalysed processes (oligomerisation, cracking and equilibration of olefins) in propane aromatisation.

Our results confirm earlier findings that H_2 pretreatment favours the formation of dispersed Ga species which possess dehydrogenation and hydrogen release properties.

The new observations are that activity and aromatics selectivity are further increased upon oxygen treatment whereas methane selectivity remains unchanged, and that only the first H_2–O_2 treatment affects dramatically the catalysts performance.

H_2–O_2 pretreatment thus appear to be a promising way to preactivate and stabilise Ga-modified aromatisation catalysts in commercial operation.

4. Conclusions

We have studied the effect of H_2–O_2 pretreatment on the catalytic performance of Ga/H-ZSM-5 catalysts used to aromatise propane.

Successive H_2–O_2 pretreatments at 823 K affect dramatically the catalytic performance, the major effect being observed for the first H_2–O_2 cycle. The first treatment in hydrogen increases activity and aromatics selectivity, and reduces methane formation. The subsequent first treatment in oxygen does not affect methane selectivity but boosts further activity and aromatics selectivity.

The effect of hydrogen is clearly to increase the dispersion of the gallium modifier, thereby generating more dual active sites combining intimately gallium species [(Ga^{3+}, O^{2-}) ion pairs) and Brönsted sites from the zeolite, enhancing overall catalytic performance, and dispersed gallium species acting as portholes to release dihydrogen, thus reducing methane production. The effect of oxygen may be to stabilise and anchor these highly dispersed gallium species, in addition to reoxidising them to the 3 + oxidation state which appears to be responsible for their optimum activity. The latter implies that gallium species cycle between the Ga(III) and Ga(I) states under these reaction conditions.

Pretreating Ga/H-ZSM-5 zeolites firstly in hydrogen and secondly in oxygen at about 800–850 K appears as a promising and convenient way to preactivate and stabilise them as catalysts prior to their use in aromatisation units. The induction period observed in the absence of such pretreatment is eliminated.

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