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Gallium based MFI zeolites for the aromatization of propane

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1. Introduction

The catalytic aromatization of light alkanes over pentasil based catalysts has been greatly studied in the recent past. Since the ''cyclar process'' has been patented, much basic research has been devoted to the study of catalysts composed of either gallium, zinc or platinum associated with an acidic form of zeolite such as ZSM-5, these composite catalysts being much more active and selective towards aromatics than the parent H-ZSM-5 zeolite.

Among the question we have addressed are:

1. What are the respective roles of the additive (Ga, or Zn or Pt) and of the acidic zeolite support?
2. What is the reaction pathway to transform propane into aromatics?
3. What are the main causes of deactivation of the catalyst?

2. Results and discussion

Most of the results have been obtained using H-ZSM-5 (Si/Al = 15 to 60) which were synthesised as described in the literature.

Gallium (gallium nitrate) was generally deposited on the zeolite support by the incipient wetness impregnation technique followed by drying at 373 K and activation under O_2 at 773 or 823 K. Before discussing the results obtained with Ga_2O_3/H-ZSM-5 catalysts it is of interest to mention that Ga_2O_3 can selectively dehydrogenate short alkanes into the corresponding olefins [1]: at 773 K, atmospheric pressure, propane is dehydrogenated into propene with a high selectivity (91%) but at a rather slow rate (0.1 mmol h^{-1} m^{-2}); similarly, hexadiene is transformed into benzene (65% selectivity) cyclohexane into benzene (87%) and more interesting, *n*-hexene into benzene (68%) suggesting that the C_6 olefin is dehydrogenated into a diene, a triene and then cyclised before being dehydrogenated to benzene. From this study it appears that gallium oxide Ga_2O_3 has, for the dehydrogenation of

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Table 1
Propane reaction over Ga/H-ZSM-5: effect of Ga content

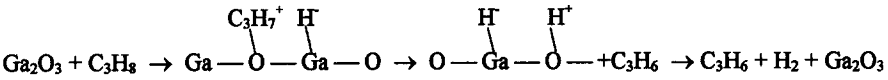
	Ga (wt%)						
Catalyst: Ga/H-ZSM-5 (Si/Al = 15)	0	0.25	1	2.5	5	1 wt% [a]	1 wt% [b]
Propane conversion (%)	0.9	2.6	4.4	5	4.4	5.6	0.3

[a] Introduced by ionic exchange.

[b] Sample a in which protons have been reexchanged with Na^+.

Temperature of reaction, 773 K; $P_{C_3H_8} = 101$ kPa; time on stream, 3 min. All samples were calcined under O_2 ($T = 773$ K), flushed with N_2 and then propane transformation was studied.

alkanes, properties similar to that of ZnO. It has also been shown [2] that reduced Ga_2O_3 is able to dissociate H_2 into H^+ and H^-; these two entities are observed by IR spectroscopy (formation of OH at 3640 cm^{-1} and of Ga^{x+}–H^- at 2020 cm^{-1}) and the assignments of these species have been confirmed by replacing hydrogen with deuterium. By analogy with the previously proposed mechanism for the activation of propane over ZnO, one can assume for Ga_2O_3 the following scheme:



$$Ga_2O_3 + C_3H_8 \rightarrow Ga-\overset{C_3H_7^+}{O}-\overset{H^-}{Ga}-O \rightarrow O-\overset{H^-}{Ga}-\overset{H^+}{O}-+C_3H_6 \rightarrow C_3H_6 + H_2 + Ga_2O_3$$

Knowing that gallium oxide is able to activate hydrocarbons or H_2, we will now review the results obtained by associating Ga_2O_3 with an acid solid such as H-ZSM-5.

2.1. Respective roles of Ga_2O_3 and H-ZSM-5 in Ga_2O_3/H-ZSM-5 catalysts

The addition of gallium to an acid H-ZSM-5 has a beneficial effect on both activity and selectivity for short alkanes cyclisation. Different methods have been used to add Ga_2O_3: among these are:

1. Impregnation of H-ZSM-5 with gallium nitrate and calcination at high temperatures (773–873 K).
2. Ion exchange with an aqueous solution of gallium nitrate.

Table 1 shows that the samples which contain Ga experienced a significant increase in activity for propane aromatization [3].

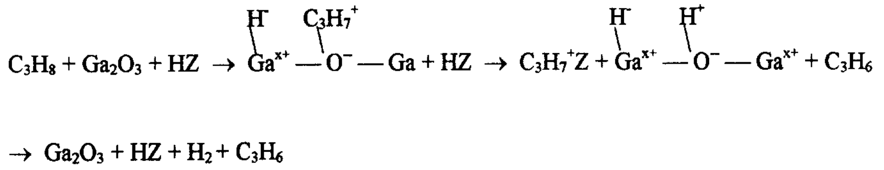
Table 1 also indicates that for the zeolite used (Si/Al = 15) there is an increase of activity up to 2.5 wt% Ga. It is of interest to observe that for the 1 wt% sample prepared by ionic exchange, the activity is better than for 1 wt% Ga deposited by impregnation suggesting that the Ga dispersion is an important factor. More interesting is the observation that if the exchanged 1 wt% Ga H-ZSM-5 is transformed via exchange with NaCl to 1 wt% Ga Na ZSM-5 the propane conversion decreases to 0.3% compared to 5.6% initially. The large difference in activity observed for 1% Ga H-ZSM-5 (exchanged sample) and 1% Ga Na ZSM-5 (exchanged sample) clearly indicates that both sites (Ga sites and protons) are needed to obtain an active catalyst; in addition, we have shown [4] that the inactive Ga Na ZSM-5 can be reactivated by back exchanging Na^+ with H^+.

From these observations we have concluded that the active site for the propane activation is a dual site composed of a Ga^{x+} ion and of a proton and by analogy with the activation of propane over Ga_2O_3 we have postulated that on Ga/H-ZSM-5 propane is activated via the following steps [4,5]

1. hydride abstraction by Ga^{x+} ion and formation of $C_3H_7^+$ adsorbed either on an oxygen ion of Ga_2O_3 or on an oxygen ion of the zeolite;

2. decomposition of $C_3H_7^+$ into H^+ and C_3H_6 on the zeolite;
3. elimination of H_2.

On Ga_2O_3/H-ZSM-5 the following equations were proposed:



$$C_3H_8 + Ga_2O_3 + HZ \rightarrow \overset{H^-}{Ga^{x+}}-\overset{C_3H_7^+}{O^-}-Ga + HZ \rightarrow C_3H_7^+Z + \overset{H^-}{Ga^{x+}}-\overset{H^+}{O^-}-Ga^{x+} + C_3H_6$$

$$\rightarrow Ga_2O_3 + HZ + H_2 + C_3H_6$$

In this scheme, the ionic state of Ga is not known but could be either Ga^{3+} or Ga^{1+} since both states exist for this compound; indeed, if the Ga ion is in an exchange position the reaction scheme should be the same.

The presence of Ga^{1+} in an ionic exchange position has been evidenced indirectly by Price et al. using mechanical mixtures of Ga_2O_3 and H-ZSM-5 submitted to reducing conditions, or using Ga_2O_3 deposited on H-ZSM-5 [6]a.

The presence of Ga^{x+} ions in an exchange position has also been confirmed using IR spectroscopy [6]b by showing that after impregnation of the H-ZSM-5 support with a gallium salt and its decomposition followed by reduction, the remaining number of protons is decreased due to the reaction:

$$Ga_2O_3 + 2H_2 + 2HZ \rightarrow 2GaZ + 3H_2O$$

The decrease of protons will depend, following the above equation, on the relative number of Ga atoms and H^+ present on the zeolite. If the number of Ga ions is larger than the total number of protons, the remaining acidity of the solid may decrease to zero.

It is of interest to note that in such a case, the activity of the solid for the propane aromatization is quite small [3] confirming that the active site is a dual site composed of a Ga ion and a proton. It is worthwhile to point out that the same picture is valid for zinc based catalysts: when protons in an H-ZSM-5 were exchanged for 0.5 wt% Zn the resulting solid was active for propane cyclisation; by contrast if the same amount of zinc is exchanged Na-ZSM-5, the resulting solid is inactive [5]. Since in both cases it is known that zinc is in exchange position as Zn^{2+}, this clearly indicates that, as for gallium, Zn^{2+} in order to be active for propane aromatization, requires the presence of a proton.

The gallium migration from the external surface of the zeolite grain to the interior of the grain occurs either on reducing conditions [5–7] or on propane reaction since this reaction is also forming hydrogen. XPS measurements have shown [7,8] that Ga ions migrate during the reduction process from the external surface of the zeolite grain to the interior of the grain, the driving force being the protons [6]a.

The gallium migration phenomenon from the external to the internal surface clearly occurred for these samples prepared by the impregnation technique or by mechanical mixture of gallium oxide and zeolite. In gallium exchanged H-ZSM-5, the position of the gallium species (external or internal surface) will depend on the pH of the solution employed for the exchange, on the concentration of Ga in the solution, high pH and high Ga concentration favouring the formation of clusters $(Ga\text{–}O\text{–}Ga)_n^{m+}$ thus favouring the location of Ga^{3+} species on or near the external surface. By contrast at low pH, low Ga^{3+} concentration, Ga^{3+} single cations are localized in the internal cationic position and in such a case reduction of Ga^{3+} into Ga^+ by H_2 would generate $2H^+$ per Ga^{3+} reduced. The reverse oxidation of Ga^+ into Ga^{3+} should remove these protons.
]

The change in acidity as a function of the Ga loading and the nature of the thermal treatment remains controversial. We have shown indirectly by using IR spectroscopy of the OH groups at room temperature that there is a definite decrease in their concentration [6]b when Ga_2O_3-H-ZSM-5 samples were reduced in H_2. By contrast Meitzner et al. [9] from the EXAFS measurements at high and low temperatures concluded that the reduced gallium species Ga^+ were reoxidized to Ga^{3+} upon cooling the sample from 773 K, temperature of reduction, to room temperature thus consuming some protons.

However, reduction of this sample without the formation of water, again converted Ga^{3+} into Ga^+ and generated H^+ species.

The authors concluded that within the experimental conditions of the reaction, that is high temperature, no decrease in the H-ZSM-5 acid site density occurred.

The apparent contradiction may result from the structure of the so called gallium-HZSM-5 catalysts.

For a sample from a true exchange mechanism that is Ga^{3+} + 3H-ZSM-5 (Ga^{3+}-ZSM-5 which would consume $3H^+$ per Ga^{3+} exchanged, reduction at high temperature would generate Ga^+ and $2H^+$ such that the initial acidity of the solid H-ZSM-5 will be little changed. Reoxidation at room temperature of Ga^+ to Ga^{3+} will considerably decrease the acidity as indicated in [9].

This possible reoxidition process could explain the contradiction between our IR results (obtained at room temperature) and the EXAFS results published by Iglesia et al. [9].

In fact, for catalytic purposes, the interesting point is to know if there is any change in the acidity at the reaction temperature (723–873 K).

Again, there is no agreement in the literature: Iglesia et al. [9], using 2-methyl-2-pentene isomerisation at 448 K or Guisnet et al. using *m*-xylene isomerisation [10] have concluded that there is no important change in the number of acid sites.

By contrast we have shown that in a true kinetic regime, the isomerisation rate of *m*-xylene [11] or the dealkylation rate of ethylbenzene [12] are strongly depressed by the addition of gallium to an H-ZSM-5 zeolite (Table 2).

Our results (decrease in the number of acid sites due to the addition of gallium) are also in good agreement with the results reported for propane aromatization which clearly indicated a decrease in aromatization activity.

In the last study (dealkylation of ethylbenzene) it has been evidenced that the migration of the gallium inside the zeolite pores causes a small decrease (≈ 10%) in the sorption capacity, but obviously the decrease of the rate of the reaction is considerably larger than the small change in the zeolite pore volume.

Thus, concerning the change in acidity of the zeolite due to the addition of gallium and to the reducing treatment our results conclusively state that the zeolite acidity decreases upon H_2-reduction of Ga_2O_3/H-ZSM-5. This decrease in acidity could be explained by assuming that, as proposed by

Table 2
Change in the isomerisation activity (*m*-xylene) and dealkylation activity (ethylbenzene → benzene + ethylene) as a function of the thermal treatment

Treatment		Rate of isomerisation [a] 5% Ga H-ZSM-5 (Si/Al = 13)	Rate of dealkylation [b] 5% Ga H-ZSM-5 (Si/Al = 16)
O_2	873 K	1	1
H_2	873 K	0.1	0.25

[a] Isomerisation of *m*-xylene $T \approx 523$ K, arbitrary units.

[b] Dealkylation of ethylbenzene $T \approx 623$ K, arbitrary units.

Table 3
Change in the propane conversion for different catalysts submitted to successive thermal treatments under O_2 or H_2

Sample	Propane conversion [a] (%) and treatment [b]					H_2
5 wt% Ga/H-ZSM-5	O_2	H_2	O_2	H_2	O_2	
Si/Al = 15	2.1	0.5	2	0.48		
Si/Al = 30	0.55	0.28	0.83	0.27	0.87	0.28
Si/Al = 60	0.21	0.33	0.53	0.42	0.55	0.43

[a] Experimental conditions: catalyst weight, 10 mg; flow rate, 4 l/h; $P_{C_3H_8} = 101$ kPa.
[b] Thermal treatment at 873 K, 1 h for O_2, 3 h for H_2.

Price et al. [6]a, Ga_2O_3-H-ZSM-5, if reduced, gives Ga ZSM-5, Ga being in the Ga^{1+} state in the exchange position, the consequence being the consumption of one proton per Ga. There is no in situ characterization report and that is why it is difficult to know if both Ga^{3+} and Ga^{1+} exist in the working catalyst and what their respective properties for propane activation are. In addition, if it is known that after a reductive treatment of Ga H-ZSM-5 part of Ga is at Ga^{1+} the other part could exist probably as the Ga^{3+} ion and/or as Ga_2O_3 well dispersed in the zeolite channels [13].

For low Ga loadings (0.5 to 2.5 wt% Ga) deposited on H-ZSM-5 (Si/Al = 15) it is observed that successive O_2 and H_2 treatments ($T = 773$ K) gradually increase the activity for propane reaction [14] before reaching a plateau, suggesting that the dispersion of Ga is gradually increased with the number of oxidative and reducing treatments. For these Ga loadings the nature of the final treatment (oxidative or reducing) do not dramatically change the rate of propane transformation; these results could indicate that Ga^{3+} and Ga^{1+} (Ga^{3+} probably exists after the oxidative treatment and Ga^{1+} after the reducing treatment) behave similarly for propane activation providing that protons still exist. In contrast are the results observed for the highest Ga loading for which, after the reducing treatment most of the protons have disappeared due to the reduction of Ga_2O_3 to Ga^{1+} followed by the exchange of H^+ for Ga^+. The factors affecting the migration of Ga ions inside the zeolite pores have not been clearly identified but it can be pointed out that the Si/Al ratio of the zeolite is probably an important parameter: the comparison between three different H-ZSM-5 zeolites (Si/Al = 15, 30 and 60) having the same Ga loading (5 wt%) indicated different behaviours (Table 3). For the sample having the highest initial acidity, steady state under O_2 (or H_2) was obtained after the first treatment (O_2 or H_2).

In addition the reduced sample is much less active than the oxidized sample; for the H-ZSM-5 having the lowest initial acidity, steady state was gradually obtained by increasing the number of treatments and the reduced catalyst was slightly less active than the oxidized one. For the sample having a medium acidity (Si/Al = 30) the behaviour in between that of the previous solids. It would be of interest to know (e.g. by XPS) the Ga distribution in the zeolite grain but unfortunately these data are missing rendering a more precise discussion difficult.

In all the catalytic experiments we have reported, care has been taken to avoid any physical change of the catalyst due to the reaction and that is why the propane reaction was performed at moderate temperature (773 K), low conversions and short time on stream (2 to 3 min).

Indeed if these conditions are not fulfilled there is a dramatic change in the catalytic properties of the solids due to a change of their nature as we will see below: recently, Hutchings et al. [15] proposed that new highly active sites for propane aromatization are formed on mechanical mixtures of gallium oxide and of H-ZSM-5 zeolite, these sites do not have the same nature than those we described earlier (Ga ion + proton).

To ascertain their proposition, they compared the catalytic properties of mixed solids (Ga_2O_3 + H-

Table 4
Conversion of propane at 773 K. Catalyst weight, 20 mg. Flow rate, 2–10 l/h. $P_{C_3H_8} = 101$ kPa. Sample 10% Ga_2O_3 + 90% H-ZSM-5 (Si/Al = 15) [16]a

Treatment [a]	Rate of propane transformation (u.a)	Aromatics selectivity (%) C basis
A	33	0.5
B	35	0.8
C	100	18
D	97	15

[a] Treatment A: calcination under a flow of oxygen at 773 K overnight. Treatment B: treatment A + calcination 1 h at 873 K under O_2. Treatment C: treatment B + reaction of propane for 5 min at 873 K. Treatment D: treatment B + reduction under H_2 at 873 K for 5 min.

ZSM-5) in propane transformation at 873 K temperature at which a physical transformation of the catalyst is likely to occur as we have shown later [16] (Table 4).

It appears clearly from this table that the H_2-treated sample behaves like the sample having reacted propane at 873 K for 5 min showing that the solid is transformed under the reactant. It was later argued [16] that experimental conditions we have used here (Table 4) are different from those used in [15] mainly because the weight ratio of propane/weight of gallium is much higher here; as a consequence the above experiments were repeated using a lower weight of propane/weight of Ga. The results reported in Table 5 have exactly the same trend as those of Table 4 and clearly evidence the transformation of the solid under propane reaction; so far, there is no experimental evidence that a mechanism different from that involving a dual site is operating.

2.2. Reaction pathway

In the previous section we have tentatively discussed the nature of the active site for propane activation giving as primary products, propene and hydrogen. As shown before, Ga_2O_3 is only able to catalyse this first step of the reaction, the second step (increase of the chain length) requiring the presence of a proton. The catalyst needs to be acidic in order to promote this oligomerisation reaction. In the temperature range used for the aromatization of propane, the propene molecules are, via alkylation isomerisation and cracking reactions, transformed into light products ($C_{2=}$) and a mixture of higher olefins (C_6–C_{9-10}) these reactions being purely acid catalyzed reactions. The next step of the reaction is more questionable since the presence of gallium could help either the dehydrogenation of naphthenes formed on acid sites via the cyclisation of the corresponding olefins as proposed by Guisnet et al. [17]a or acts as a dehydrogenation catalyst to transform the long chain olefins into dienes (and possibly trienes) before there cyclisation on the acid sites as we have demonstrated [17]b:

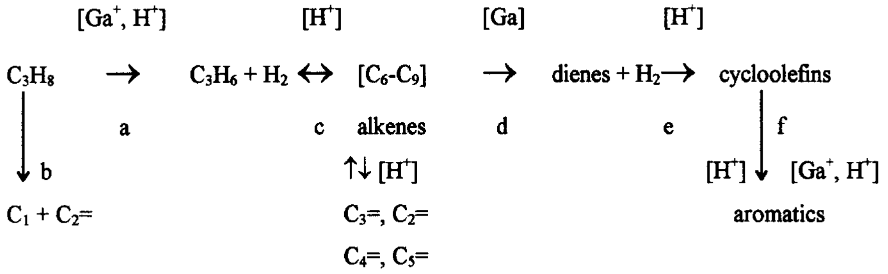
In order to clear up this question we have compared the rate of benzene (or toluene) formation

Table 5
Reaction of propane at 500°C over 10% Ga_2O_3 + 90% H-ZSM-5 (Si/Al = 15). Catalyst weight, 10 mg. Flow rate, 3 l/h. $P_{C_3H_8} = 20$ kPa. Time on stream, 2 min

Treatment [a]	Conversion (%)	Aromatic selectivity (%) C basis
A	1.7	1
B	1.7	0.9
C	4.3	12
D	5.4	14

[a] Treatment A: O_2 overnight at 773 K. Treatment B: A + O_2 1 h at 873 K. Treatment C: B + reaction of propane at 873 K for 5 min ($P_{C_3H_8} = 0.2$. Atmosphere flow rate, 1.5 l/h). Treatment D: H_2 ($p = 7$ kPa for 3 min at 873 K).

starting from different precursors such as *n*-hexene, hexadiene, cyclohexane, cyclohexene... on 2 wt% Ga/H-ZSM-5 (Si/Al = 30) catalysts either in the absence or in the presence of hydrogen: thus, in the absence of hydrogen (corresponding to low propane conversion) or in the presence of hydrogen (corresponding to high propane conversion) the results clearly indicate that in any case the alicyclics are intermediates since the rate of benzene formation is larger for *n*-hexene than for cyclohexane or methylcyclopentane. Thus, it was concluded that dienes are intermediates. When dienes are formed, it has been shown that in the absence of H_2, trienes are likely intermediates but in the presence of hydrogen, dienes are cyclised into cycloolefins before being dehydrogenated. The following reaction pathway has been proposed [17]b, step a governing the rate of propane transformation.



The general reaction pathway established above corresponds to a well balanced Ga/H-ZSM-5 catalyst; in the case of a catalyst having a low Ga loading on an highly acidic zeolite (balance in favour of the acid function) the reaction pathway could be different.

Kinetic studies have shown that the rate of propane transformation over Ga/H-ZSM-5 catalyst has an order of 0.6 to 0.7 with respect to propane, and a negative order with respect to H_2. The orders of the reactions over a pure acid solid like H-ZSM-5 (Al or Ga) are 1 for propane and zero for hydrogen [18]; it has been shown that these results (relative orders) are of interest to discriminate between gallosilicates (MFI structure) having no extra framework Ga and which are poor aromatization catalysts and gallosilicates having extra framework Ga which are much better aromatization catalysts.

2.3. Deactivation of the catalyst: main causes

It was observed that the Ga/H-ZSM-5 catalyst deactivates with time on stream [19,20]: as an example, after 2 h on stream at 823 K a decrease of nearly 35% was observed for an initial conversion of 28% (atmospheric pressure of propane) [19], at this stage the colour of the catalyst was deep black indicating a coke deposit. The catalyst can be reactivated by burning these carbon deposits in air and CO_2 and H_2O are formed, this later compound could be responsible of the partial dealumination of the zeolite support if the regeneration temperature is too high [20]. In addition to poisoning the active sites (see below) this coke deposit is the cause of partial pore blockage as observed by the decrease of the sorption capacities [20].

Since Ga/H-ZSM-5 catalyst has two different types of sites (Ga^+ sites and protons) it is of interest to know if during ageing both types of sites are equally deactivated. Using pyridine adsorption on fresh and aged solids, to probe their acidity we have shown that the Brönsted acidity is more depressed by the coking than the Lewis acidity (Ga^+ sites) [19]; considerations on the change of selectivity with time on stream (assuming that the methane is mainly formed on Brönsted sites) are in good agreement with the above conclusions.

Another parameter could also be the cause of the deactivation of Ga/H-ZSM-5 catalysts, in particular for samples having high Ga loading [e.g. 5% Ga/H-ZSM-5 (Si/Al = 15)]: we have shown that, after hydrogen reduction, the acidity of such a solid is smaller than the activity of the oxidized sample. Since hydrogen is the major product of the propane transformation (on a molecular basis), this phenomenon could play a role in the ageing. So we have shown [7] that at 773 K both phenomena, coke formation and hydrogen production, are the cause of the deactivation, the coke deposit causing, at the beginning of the reaction (0–30 min) on stream a larger deactivation than the transformation of the solid under hydrogen.

In all cases, if the TOS (time on stream) is relatively short, 2 to 3 h, the regeneration under air or oxygen is very effective and the catalyst is able to be regenerated and recycled for a large number of runs (21).

3. General conclusions

For the three question we addressed, we have been able to conclude:

1. The active site for propane activation (formation of propene) is a dual site (Ga^{x+}–H^+), x being either 1 or 3. Since gallium addition to H-ZSM-5 catalyst decreases the number of available protons, the gallium content has to be adjusted to the number of protons of the starting material in order to have a good balance between the Ga^{x+} ions and the remaining number of protons.
2. The formation of aromatics is the result of the propane dehydrogenation (on Ga^x+, H^+), oligomerisation of propene (on H^+), dehydrogenation of these high olefins (on Ga^x+, H^+), cyclisation into cycloolefins (on H^+) and dehydrogenation of the cycloolefins into aromatics on (Ga^{x+}, H^+).
3. The deactivation of the catalyst with TOS is due to coke formation causing a partial pore blocking and a poisoning of both sites, Ga^{x+} ions and protons; the acid function is more deactivated than the dehydrogenating function.

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