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Temperature Programmed Oxidation of Coked H-Gallosilicate (MFI) Propane Aromatization Catalyst: Influence of Catalyst Composition and Pretreatment Parameters

V. R. Choudhary,*[,1] P. Devadas,* S. D. Sansare,* and M. Guisnet†

**Chemical Engineering Division, National Chemical Laboratory, Pune-411 008, India; †URA CNRS-350, Catalyse en Chimie Organique, Universite de Poitiers, 40 Avenue du Recteur Pineau, 86022 Poitiers Cedex, France*

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Temperature programmed oxidation (TPO) of H-gallosilicate (MFI) coked in the propane aromatization at 550°C for a time-on-stream of 7–8 h has been investigated by measuring point to point the consumption of oxygen and also the formation of the both CO and CO_2 (by GC analysis using a 16-loop gas sampling valve) during the TPO run from 50° to 900°C at a linear heating rate of 20°C min^{-1} in a flow (50 cm^3 min^{-1}) of a O_2–He mixture (8.0 mol% O_2). The Si/Ga and Na/Ga ratios, calcination temperature, and hydrothermal pretreatments of the zeolite and also the presence of binder (silica or kaolin) in the catalyst have a strong influence on the TPO of coked zeolite. The influence is attributed to changes in the zeolite properties (viz., zeolitic acidity or framework Ga and non-FW Ga-oxide species), which affect the coke oxidation both directly and/or indirectly, by controlling the nature of coke formed during the coking process. © 1997 Academic Press

INTRODUCTION

H-Gallosilicate (MFI) zeolite shows high activity/selectivity in the aromatization of lower alkanes (1–7), which is a process of great commercial importance. However, this zeolite catalyst undergoes fast deactivation due to coking in the propane aromatization (3, 4, 7). The deactivated zeolite can be fully regenerated by removing the coke deposited on the zeolite by oxidative treatment, under controlled conditions (7, 8). The activity of the zeolite is not decreased after subjecting it to a number of regeneration cycles (8).

Temperature programmed oxidation (TPO) technique has been used earlier for investigating oxidation of coke on a number of catalysts such as Pt/Al_2O_3 (9, 10), Ni/Al_2O_3 (11), $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ (12), HY and H-ZSM-5 zeolites (13). However, as compared to temperature-programmed reduction (TPR) (14), the work reported on TPO is, in general, very small.

A few studies have been reported on the oxidation of coked zeolite catalysts. In the oxidation of coke on HY, H-mordenite (HM), and H-ZSM-5, Magnoux and Guisnet (15) observed that the oxidation rate depends very little on the coke content but is strongly dependent on the zeolite; it is higher on HY and HM than on H-ZSM-5. Similar observation has also been made by Novakova and Dolejsek (13) in their studies on the TPO of coked HY and H-ZSM-5. However, a little or no information is available on the oxidation of coked H-gallosilicate (MFI) zeolite.

H-gallosilicate (MFI) zeolite contains both framework Ga and extra framework Ga-oxide species, which are formed during the synthesis and/or pretreatment of the zeolite (3, 6, 7, 16–20). Hence, it is interesting to know the influence of the framework Ga (which is responsible for zeolitic acidity) and nonframework Ga-oxide species on the oxidation of coked H-gallosilicate. The present work was undertaken for this purpose. In this paper, the influence of zeolite composition (viz. bulk Si/Ga and Na/Ga ratios, FW and non-FWGa and binder, such as silica, and kaolin) and pretreatment parameters (viz., calcination temperature and hydrothermal pretreatment) on the TPO of coked H-gallosilicate (MFI) has been thoroughly investigated.

EXPERIMENTAL

The bulk and framework composition of H-gallosilicate zeolites having MFI structure (H-GaMFI) and their thermal or hydrothermal pretreatment before coking are given in Table 1. The preparation and characterization of the zeolites with different bulk Si/Ga and Na/Ga ratios and those pretreated under different thermal and hydrothermal conditions are given in our earlier papers (7, 18–20). The binder containing zeolite catalysts (Table 2) were prepared by physically mixing powdered binder (viz. silica gel (Fuji Davison), or kaolin) and NH_4-GaMFI (Si/Ga 39.5 and Na/Ga = 0.03) zeolite (binder/zeolite (wt/wt) ratio = 1.0), pressing and crushing to 0.2–0.3 mm size particles and finally calcining at 600°C under N_2 flow for 1 h. The strong acidity of all the zeolite catalysts (before coking) was

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[1] To whom correspondence should be addressed.

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TABLE 1

Results of TPO for Coked H-GaMFI Zeolite (without Binder) Having Different Composition and Pretreated under Different Conditions before Coking in the Propane Aromatization

Bulk composition		Pretreatment conditions[a]		Strong acidity (mmol. g^{-1})	Ga (p.u.c.)		Carbon deposition (mmol.g^{-1})		TPO peak max. temp (°C)	CO_2 /CO ratio		O_2 consumption (mmol.g^{-1}) for				H/C ratio in coke
Si/Ga ratio	Na/Ga ratio	Temp (°C)	Concn. of steam (mol%)		FW	Non-FW	MA[b]	TPO		At peak max.	In overall TPO	CO form-ation	CO_2 form-ation	Oxidn. of reduced Ga-species	H_2O form-ation	
33	0.09	600	0.0	0.30	1.86	1.01	2.70	2.70	640	3.8	3.1	0.33	2.04	0.09	0.47	0.70
51	0.05	600	0.0	0.26	1.53	0.34	1.64	1.63	633	1.2	1.2	0.37	0.89	0.03	0.37	0.91
129	0.05	600	0.0	0.13	0.71	0.02	0.18	0.16	440	0.0	0.0	0.08	0.00	0.002	0.06	1.50
33	0.45	600	0.0	0.16	1.86	1.01	1.46	1.29	633	1.2	1.1	0.31	0.67	0.09	0.36	1.12
33	0.09	750	0.0	0.09	0.85	1.95	1.18	1.08	600	3.3	2.0	0.18	0.72	0.17	0.29	1.07
33	0.09	400	48	0.25	2.18	0.64	2.06	1.96	633	5.0	3.3	0.23	1.50	0.06	0.42	0.86
33	0.09	600	13	0.15	1.68	1.14	1.36	1.35	592	4.6	3.0	0.17	1.01	0.10	0.40	1.19
33	0.09	600	80	0.05	0.44	2.38	0.32	0.20	400	0.0	0.0	0.10	0.00	---	0.08	1.60

[a] Period of the pretreatment = 4 h.

[b] MA = microanalysis.

TABLE 2

Results of TPO for Coked H-GaMFI (Si/Ga = 39.5 and Na/Ga = 0.03) Zeolite Catalysts Containing Silica or Kaolin as Binder (Zeolite/binder ratio (wt/wt) = 1)

Binder :	Silica	Kaolin	Without binder
Strong acidity (mmol.$g^{-1}_{zeolite}$)	0.05	0.14	0.25
Carbon deposition (mmol.g^{-1}) by			
Microanalysis	0.59	0.72	2.52
TPO	0.36	0.64	2.51
TPO peak max. temp (°C)	642	640	640
CO_2 / CO ratio			
Peak maximum	1.3	0.6	1.8
Overall TPO	1.0	0.6	1.6
O_2 Consumption (mmol.g^{-1}) for			
CO formation	0.09	0.20	0.48
CO_2 formation	0.18	0.24	1.55
Oxidn. of reduced Ga-oxide species	0.05	0.05	0.05
H_2O formation	0.10	0.15	0.46
H/C ratio in coke	1.11	0.94	0.73

measured in terms of the pyridine chemisorbed at 400°C using the GC pulse technique (21). The bulk chemical composition of the zeolite samples was determined by their chemical analysis. The FW Si/Ga ratio of the zeolite samples was obtained from the ^{29}Si MAS NMR (7, 18–20).

All the above zeolite catalysts were deactivated due to coking in the propane aromatization reaction at 550°C for a period of 8–10 h, using 33 mol% propane (balance N_2) as a feed at a space velocity of 3100 $cm^3\ g^{-1}\ h^{-1}$. Detailed procedure for carrying out the time-on-stream activity of the zeolite in the propane aromatization is given earlier (7). After coking, the deactivated zeolite catalysts were cooled in the flow of N_2 free from the traces of O_2 and moisture. The carbon deposition on the coked catalysts was measured by the microanalysis.

Temperature programmed oxidation (TPO) of the coked zeolites was carried out in a quartz tubular reactor (i.d.: 8 mm) containing 0.2–0.8 g coked catalyst, depending upon its coke content, in a flow (55 $cm^3\ min^{-1}$) of 8.0 mol% O_2 (balance He) from 70° to 950°C at a linear heating rate of 20°C min^{-1}. The reactor temperature was measured by Cr–Al thermocouple located in the catalyst bed. The reactor effluent gasses (i.e., the product of the TPO) are sampled at the different TPO temperatures, using a 16-loop gas sampling valve. After completion of the TPO run, the gas multiloop sampling valve was connected to a gas chromatograph with TCD. The gas samples were then analyzed for O_2, CO, and CO_2 by GC using a Spherocarb column and He as a carrier gas. The dead volume between the catalyst and gas sampling valve was small. However, a small correction to the TPO temperature was made for taking into account the dead volume. The total consumption of O_2 and its consumption for the conversion of coke to CO and CO_2 in the TPO were obtained from the analysis of the feed and products for O_2, CO, and CO_2 as follows. Total O_2 consumption (%) = [O_2 (in feed) − O_2 (in products)/O_2 (in feed)] × 100. Consumption of O_2 in the CO formation (%) = [0.5 CO (in products)/O_2 (in feed)] × 100. Consumption of O_2 in the CO_2 formation (%) = [CO_2 (in products)/O_2 (in feed)] × 100.

RESULTS

Results on the TPO of coked H-GaMFI zeolite with different Si/Ga and Na/Ga ratios, calcined at different temperatures and pretreated hydrothermally at different temperatures and steam concentrations are presented in Figs. 1, 2, and 3, respectively. TPO curves for the coked H-GaMFI catalyst containing different binders (concentration of binder: 50 wt%) are presented in Fig. 4. Data on the bulk composition, framework, and nonframework Ga, strong acidity (measured in terms of the pyridine chemisorbed at 400°C), carbon deposition on the coked zeolite catalysts (measured by microanalysis and also determined from the CO and CO_2 formed in the TPO), and their TPO peak maximum temperature and CO_2/CO product ratios (at peak maximum and in overall TPO) are given in Tables 1 and 2. The quantitative results on the O_2 consumption for the formation of CO, CO_2, and water and the oxidation of Ga_2O to Ga_2O_3, along with H/C ratio of the coke, are also included in Tables 1 and 2. The H/C ratios are obtained from the H_2O, CO, and CO_2 formed in the TPO. However, since the H_2O formed is evaluated from the O_2 balance (i.e., from the O_2 consumption, obtained by subtracting the O_2 required for the formation of CO and CO_2 and the oxidation of reduced Ga-oxide species from the total consumption of O_2) the H/C ratios may not be very accurate. Nevertheless, the H/C ratio shows a significantly large variation with a change in the zeolite composition and/or pretreatment condition.

Effect of Si/Ga Ratio

A comparison of the results in Figs. 1a, c, and d and Table 1 shows a strong influence of Si/Ga ratio on the TPO and also on the H/C ratio of coke. With the increase in the Si/Ga ratio, the TPO peak temperature is decreased and the TPO curve is shifted more and more towards low temperature side, and also the CO_2/CO product ratio (both at the peak maximum and in the overall TPO) is decreased very markedly. The H/C ratio of the coke is, however, increased. In the TPO of the coked zeolite with Si/Ga ratio

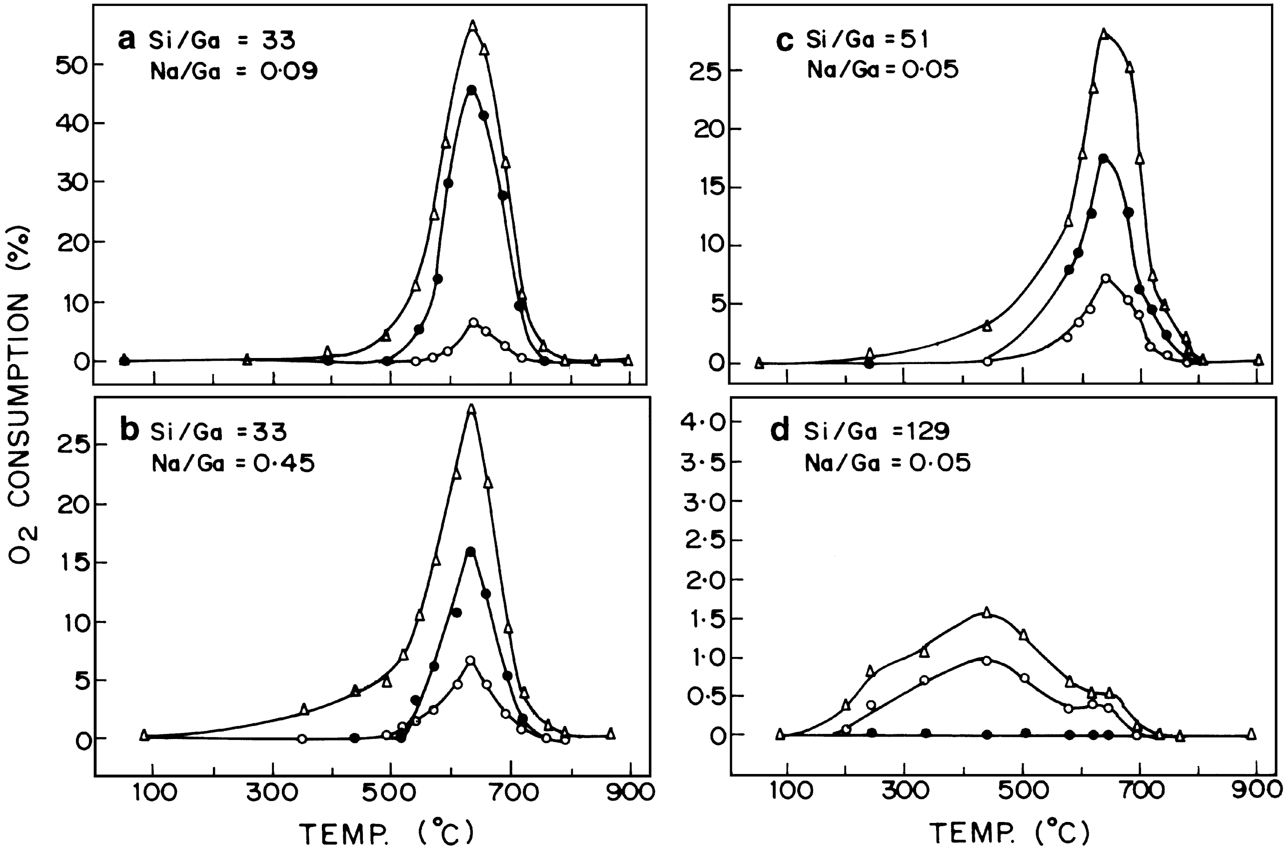

FIG. 1. TPO of coked H-GaMFI (calcined at 600°C before coking) with different bulk Si/Ga and Na/Ga ratios (△, total O_2 consumption; ○, O_2 consumption for CO formation; ●, O_2 consumption for CO_2 formation).

of 129, there is no formation of CO_2 at all; only CO is formed in the decoking. This may be due to the large decrease in both the acidity and nonframework Ga with increasing the Si/Ga ratio (Table 1).

Effect of Na Content

A comparison of Fig. 1a with Fig. 1b suggests that the increase in the Na content (increase in the Na/Ga ratio from 0.09 to 0.45) has only a small effect on the TPO peak temperature; it is decreased only by a few degrees centigrade. However, the formation of CO_2 relative to that of CO is decreased markedly and the H/C ratio of the coke is increased with increasing the Na-content and hence with decreasing the zeolitic acidity (Table 1).

Effect of Calcination Temperature

When the calcination temperature is increased from 600°C to 750°C, the H/C ratio of the coke is increased and the TPO of the coked zeolite is also affected very significantly. The TPO peak temperature is decreased; the TPO curves are shifted towards lower temperature side (Fig. 2). There is a small decrease in the CO_2/CO ratio at the peak maximum but the decrease of CO_2/CO ratio in the overall TPO is more (Table 1). However, for the zeolite calcined at higher temperature, the CO formation curve is broader than that of the CO_2 formation curve and, at lower temperature (below 500°C), there is much more CO formation as compared to the CO_2 formation (Fig. 2). This may because of the fact that the acidity is decreased and non-FW Ga is increased due to the degalliation with increasing the calcination temperature (Table 1).

Effect of Hydrothermal Treatment

A comparison of the results in Fig. 3 and Table 1 clearly shows the strong influence of hydrothermal treatment (at different conditions) on the H/C ratio and TPO of the coked zeolite. When the severity of the hydrothermal treatment (i.e., temperature and/or concentration of steam) is increased, the H/C ratio is increased, the TPO curves are shifted towards lower temperature side and are also broaden. The CO_2/CO ratio is also decreased markedly. Because of the hydrothermal treatment at the most severe conditions (80% steam at 600°C) there is a very large decrease in the peak maximum temperature and also a drastic reduction in the CO_2 formation in the TPO; only the formation of CO but not CO_2 in the oxidation of coke is observed. The increase in the severity of hydrothermal treatment also results in a decrease in the acidity and an increase in the non-FW Ga of the zeolite (Table 1).

Effect of Binder

A comparison of the results in Fig. 4 and Table 2 shows an appreciable effect of binder on the H/C ratio and TPO of the coked zeolite catalyst. For both binders, although the TPO peak maximum temperature was almost the same, the shape of TPO curve is quite different. The relative formation CO and CO_2 for these coked catalysts is also found to vary with the temperature of TPO. Particularly at the lower temperatures, only the formation of CO is observed but at the higher temperatures, the formation of CO_2 exceeds the formation of CO (Fig. 4). The H/C ratio of the coke is increased and the CO_2/CO ratio (both at the peak maximum and in the overall TPO) is decreased due to the presence of both the binders.

In all the TPO studies, it is interesting to note that, at the lower temperatures, there is a small but significant consumption of O_2 even when there is no formation of any carbon oxide (Figs. 1–4).

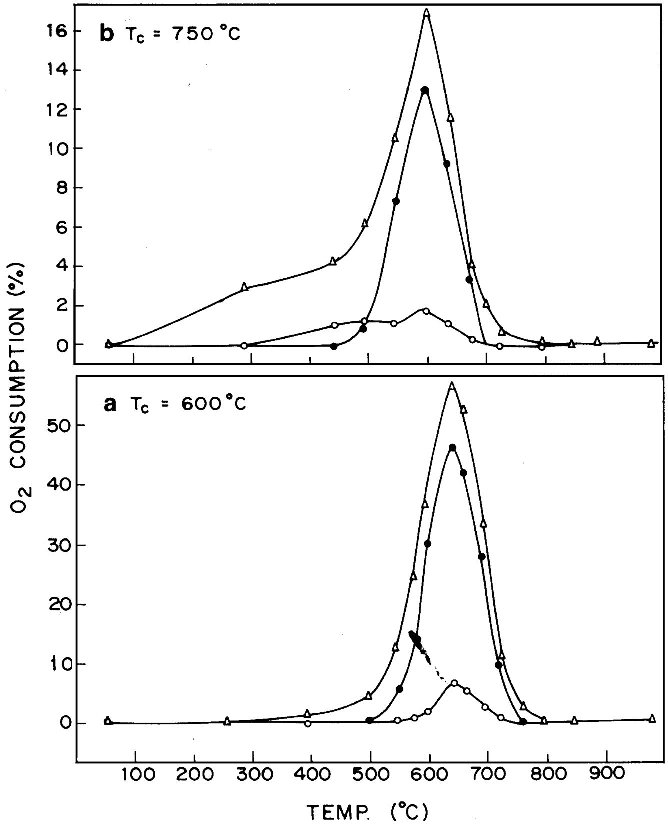

FIG. 2. TPO of coked H-GaMFI (Si/Ga = 33 and Na/Ga = 0.09) calcined at two different temperatures before coking (Δ, total O_2 consumption; ○, O_2 consumption for CO formation; ●, O_2 consumption for CO_2 formation).

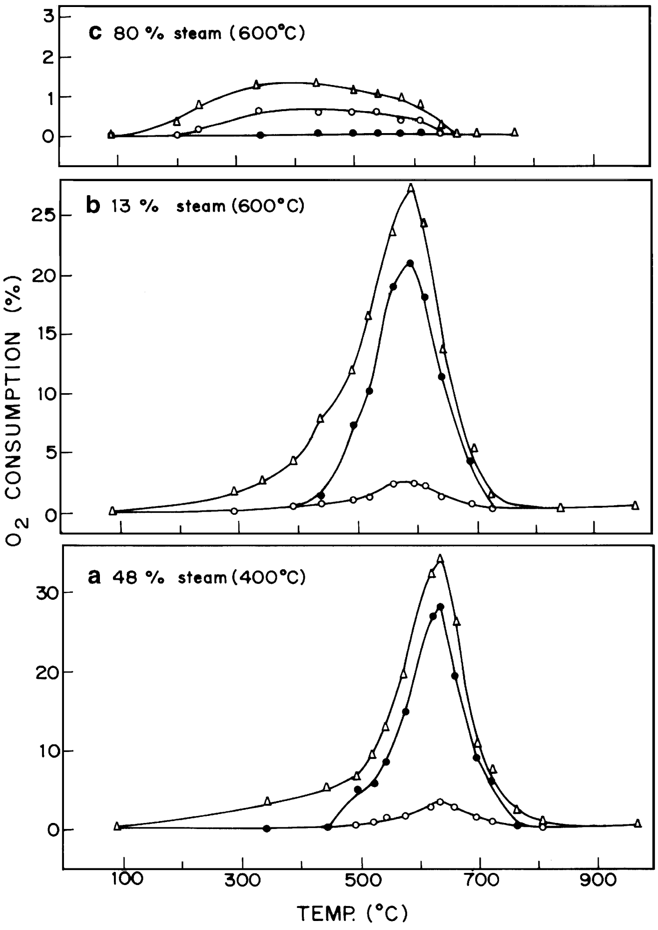

FIG. 3. TPO of coked H-GaMFI (Si/Ga = 33 and Na/Ga = 0.09) pretreated hydrothermally at different concentrations steam and temperatures before coking (Δ, total O_2 consumption; ○, O_2 consumption for CO formation; ●, O_2 consumption for CO_2 formation).

DISCUSSION

During the aromatization of propane (at 550°C), the non-FW Ga-oxide species in the zeolite are reduced by the hydrogen produced in the aromatization process. Hence, for most of the coked zeolite samples, the observed consumption of O_2 in the initial period (i.e., at lower temperatures) of TPO even in the absence of any carbon-oxide formation is expected because of the oxidation of reduced nonframework Ga-oxide species (viz., Ga_2O) present in the coked zeolite to Ga_2O_3. It can also be partly due to the oxidation of hydrogen from the coke, which occurs at temperatures lower than that required for the oxidation of carbon, and also because of the partial oxidation of coke molecules to oxygenated compounds such as aldehydes, ketones, anhydrides, phenols, etc., prior to the formation of CO and CO_2 (22).

In this investigation, it was not possible to compare the TPO of the coked zeolites samples having nearly the same

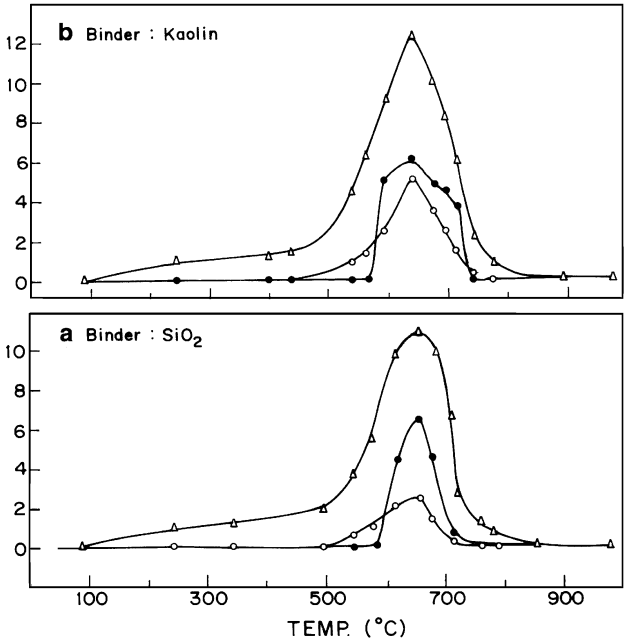

FIG. 4. TPO of coked H-GaMFI (Si/Ga = 39.5 and Na/Ga = 0.03) zeolite catalysts containing silica or kaolin binder with zeolite/binder (wt/wt) ratio of 0.1 (Δ, total O_2 consumption; ○, O_2 consumption for CO formation; ●, O_2 consumption for CO_2 formation).

coke content (Tables 1 and 2). Earlier studies (15) on the oxidation of coked HY, HM, and H-ZSM-5 zeolites had indicated that the rate of coke oxidation depends very little on the coke content. The CO_2/CO ratio in the oxidation of coked H-ZSM-5 is also found to be not affected even by a four fold change in the coke content (13). Hence, the influence of coke content on the TPO in the present case is also expected to be negligibly small and the results of TPO essentially reflect the influence of zeolite composition and pretreatment parameters on the coke oxidation. Indeed, no significant change in the peak maximum temperature and CO_2/CO ratio in the TPO is observed when the coke content of the zeolite was increased from 3.22 wt% (Table 1) to 7.82 wt% by prolonging the coking period up to 120 h in the propane aromatization under similar conditions.

In earlier studies on the oxidation of coked HY and H-ZSM-5 zeolites, the rate of coke oxidation was found to be higher on HY than on H-ZSM-5 (13, 15). The CO_2/CO ratios in the coke oxidation products were also found to be different; the CO_2/CO ratios were lower for H-ZSM-5 zeolite (13). The observed different results for the two zeolites were attributed to zeolite structure (13, 15) and density of acid sites (22); the higher the density of acid sites, the faster is the coke oxidation. The observed decrease in the CO_2/CO with increasing the Si/Ga ratio, calcination temperature, and Na content of the zeolite and also due to the presence of binder is consistent with this. However, the high acidity combined with high non-FW Ga-oxide species seems to be responsible for the high CO_2/CO ratio for the zeolite pretreated hydrothermally at 400°C and 600°C at 48 and 13 mol% steam, respectively. However, for the zeolite pretreated at very severe hydrothermal conditions (with 80 mol% steam at 600°C) or the one having higher Si/Ga ratio, the CO_2 formation in the TPO is absent. In both the cases, the zeolite has very low acidity. These observation could be explained as follows.

The influence of zeolite properties on the coke oxidation may be direct or indirect. It is indirect when the nature of coke is changed, as indicated by a significant change in its H/C ratio due to the change in the acidity and non-FW Ga of the zeolite through the changes in its composition and/or pretreatment condition. Since, the character of coke on HY and H-ZSM-5 zeolites is also found to play an important role in the coke oxidation (13), the indirect influence of the zeolite properties on the coke oxidation is important, particularly when there is a very significant change in the H/C ratio and consequently in the nature of coke, as in the case of the zeolite with very low acidity. The results show a strong influence of the zeolite composition and pretreatment parameters on the oxidation of coke and also on the zeolitic acidity and concentration of non-FW Ga-oxide species (Tables 1 and 2). When the influence of an individual parameter on the TPO is considered, both the TPO peak temperature and CO_2/CO product ratio are decreased with decreasing the zeolitic acidity. This is consistent with that observed earlier (22). However, the observed trend for the effect of acidity on the coke oxidation rate is different from the earlier one observed for the oxidation of coked HY and H-ZSM-5 zeolites (22). It may also be noted that when all the zeolite composition and pretreatment parameters are taken together, the observed above relationship of the acidity with the TPO peak temperature and CO_2/CO ratio is no longer valid. It is also not valid for the zeolite catalyst containing the two different binders. The H/C ratio is also changed very significantly due to a change in the zeolite acidity, indicating a gradual change in the nature of coke with a change in the acidity. All these observations indicates that the zeolite properties, play both direct and indirect roles in the oxidation of carbonaceous deposits (or coke) on H-GaMFI zeolite.

The indirect role of the zeolite properties is evident from a comparison of the TPO in Fig. 1a with that in Figs. 1d and 3c and the H/C ratio of the coke on the corresponding zeolites (Table 1). The TPO curves in Fig. 1a, showing the oxidative coke removal at higher temperature with high CO_2/CO ratio in the oxidation products, corresponds to a hard (highly condensed polyaromatic) or refractory coke, and as expected, its H/C ratio is lowest (0.70). Whereas, the TPO curves in Figs. 1d and 3c, indicating the coke removal at lower temperatures with the formation of CO but not CO_2 in the coke oxidation, suggest that the coke deposited is soft or volatile in nature and its high H/C ratio (1.5 and

1.6, respectively) is consistent with the volatile nature of the coke. The results also indicate that the zeolite property responsible for controlling the coke nature is mostly the zeolitic acidity.

The formation of CO in the oxidation is expected due to homogeneous oxidation of volatile coke and/or thermal decomposition of oxygenated primary products of the coke oxidation at lower temperatures. However, more condensed (i.e., nonvolatile coke) resulting from pyrolysis of coke on HY and H-ZSM-5 zeolites are burned at higher temperature (13). Hence, both the oxidation temperature and CO_2/CO product ratio in the TPO can reflect the nature of coke. Moreover, the carbon deposition determined from the formation of CO and CO_2 in the TPO is found to be somewhat lower than that measured by the microanalysis, particularly for the coke with higher H/C ratios (Table 1). The lower carbon deposition observed from the TPO is expected mainly due to a desorption of more volatile coke molecules during the TPO. This is consistent with our earlier studies (23), which showed that a major portion of the coke deposited on H-GaMFI zeolite in the propane aromatization at 400°C could be removed simply by heating the coked zeolite upto 600°C in flow of inert gas.

Location of coke (in the zeolite channels, at the outer surface of zeolite crystals, on binder, close or away from Ga-oxide species, etc.) is also expected to play an important role in the coke oxidation. The CO_2/CO ratio in the oxidation of coked H-ZSM-5 was found to be 0.3 (13), which is much lower than that observed for most of the coked zeolite samples in the present case. This indicates that the observed higher CO_2/CO ratio in the present case is mostly due to the presence of non-FW Ga-oxide species, which have redox function. Since, the coke deposited on binder is away from the non-FW Ga-oxide species, the CO_2/CO ratio in this case is expected to be lower and this is what observed (Table 2); the addition of binder caused a decrease in the CO_2/CO ratio. The results thus show that the CO_2 formation, in the coke oxidation is facilitated in the presence of the non-FW Ga-oxide species. However, it should be kept in mind that the CO_2/CO ratio depends also on the density of acid sites (22) and the coke characteristics.

The zeolite properties through their combined effect control both the nature of coke and its oxidation. Whereas, the coke oxidation also depends on the nature of coke and the zeolite properties. Hence, it is difficult know whether the observed influence of zeolite properties on the coke oxidation is due to their direct effect or because of their indirect (through a change in the coke characteristics) effect. Also, because of the combined effect of the zeolite properties on the coke oxidation, the effect of individual property is difficult to ascertain unless only one property is varied while keeping all the others the same, which is extremely difficult in the case of H-GaMFI zeolite due to its low stability for FW-Ga. Further studies are therefore necessary for clearly understanding the influence of the acidity and non-FW Ga-oxide species of the zeolite on both the nature of coke formed and its oxidation.

CONCLUSIONS

From the TPO of H-gallosilicate zeolites (with different Si/Ga and Na/Ga ratios, calcined and hydrothermally treated at different conditions and also containing different binders) coked under identical conditions in the propane aromatization, following important conclusions could be obtained.

1. The TPO with the GC analysis of CO, CO_2, and O_2 in the reaction mixture provides interesting information not only on the O_2 consumption but also on the CO_2/CO product ratios in the oxidation of coked zeolites and also on the H/C ratio of the coke.
2. The oxidation of coke on H-GaMFI zeolite is strongly influenced by the zeolite composition and pretreatment parameters; both the temperature required for the coke oxidation and the CO_2/CO product ratio are influenced. The presence of binder in the zeolite catalyst has also a significant effect on the CO_2/CO product ratio but not on the temperature required for the coke oxidation. The formation of CO_2 over CO is facilitated by the non-FW Ga-oxide species.
3. The influence of zeolite composition and pretreatment parameters on the coke oxidation is attributed to the changes in the zeolitic acidity (or FW Ga) and the non-FW Ga-oxide species. However, the coke oxidation is influenced by these zeolite properties not only by their direct effect on the coke oxidation but also indirectly by controlling the nature of the coke formed during the coking process. Influence of the zeolite properties on the coke oxidation is thus very complex, it is a result of the combined effects produced, both directly and indirectly, by both the zeolite properties.

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