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Oscillations in the catalytic oxidation of volatile organic compounds

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Abstract

The catalytic oxidation of methyl isobutyl ketone (MIBK) and *o*-xylene was studied on different catalysts. Oscillations in the molar flow rate of CO_2 were observed in some systems, corresponding to apparent conversions into CO_2 exceeding 100%. The oscillatory behaviour was found to be associated to the presence of strongly adsorbed compounds at the temperature of the reaction, which could be detected by TPO and TPD. The phenomenon is therefore determined by the strength of adsorption of the VOC in the catalyst support.

Keywords: VOC; Oxidation; Platinum/zeolite; Coke; Oscillations; Adsorption

1. Introduction

Catalytic oxidation is one of the most important technologies used for the destruction of volatile organic compounds (VOCs), especially when the VOC concentration is low, as it can treat the effluents at low/moderate temperatures, avoiding high energy costs [1–3]. Noble metals supported on alumina are the most used supported metal catalysts [4,5]; however, zeolites have already proven to be good supports for the catalytic oxidation of aromatics [6–8] and chlorinated VOCs [9,10].

Oscillatory behaviour in oxidation reactions is a well-known phenomenon which has been reported several times, particularly in the case of CO oxidation by noble metal catalysts [11–15]. Oscillations in the combustion of heptane were also observed over a Pt/Al_2O_3 catalyst [16] under some specific reaction conditions and also in the oxidation of methane over a Pd/Al_2O_3 catalyst [17]. This phenomenon is frequently explained in terms of the oxidation state of the noble metal, by a mechanism where the metal changes from the reduced to an oxidised form, the later being less active. The metal is oxidised by oxygen and reduced by the hydrocarbon, cyclically, so that it becomes successively less and more active, originating the oscillatory behaviour.

In a previous study [18], it was shown that oscillations in the apparent conversion into CO_2 occurred in the oxidation of methyl isobutyl ketone (MIBK) over a Pt/HFAU zeolite. The fact that apparent conversions into CO_2 higher than 100% were observed ruled out the explanation given above. In this case, the oscillations were caused by the oxidation of some nondesorbed compounds that were trapped in the zeolite pores during the reaction.

Apparent conversions into CO_2 higher than 100% were also observed by Paulis et al. [19]. These authors studied the oxidation of toluene and acetone over supported Pd and Mn_2O_3 catalysts. Disagreements were found between the conversion of the VOC and the CO_2 released when performing temperature programmed oxidation of the VOCs. At the beginning of the experiments, at low temperatures, it was observed that the conversion of the VOC was higher than the conversion into CO_2. This was explained by the retention of part of the VOC in the catalyst. As the temperature increased, a CO_2 peak was observed in the ignition curve, corresponding to conversions into CO_2 higher than 100%. These results were explained in terms of the adsorption–desorption processes occurring in the catalyst [19].

The aim of the present investigation is to gain a deeper understanding of the oscillatory behaviour observed in the oxidation of VOCs. For that purpose, the oxidation of

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MIBK and *o*-xylene was studied over two Pt/zeolite catalysts (Pt/HFAU and Pt/NaFAU) as well as over NaFAU and Pt/γ-Al_2O_3. TPO and TPD were also carried out after reaction in order to gain better insight into the nature of the compounds that remain adsorbed in the support. In the case of MIBK, the oscillatory behaviour was observed with all the zeolite catalysts but not on Pt/γ-Al_2O_3. With *o*-xylene, oscillations were observed with the Pt/NaFAU catalyst and not with Pt/HFAU catalyst. These oscillations are a consequence of the oxidation of compounds that remain adsorbed inside the zeolite pores, including the reactant; therefore, the strength of adsorption of the VOC on the support seems to be the major parameter which determines the oscillation phenomenon.

2. Experimental

2.1. Preparation and characterisation of the catalysts

HFAU zeolite (framework Si/Al ratio of 47) was supplied by PQ zeolites, NaFAU zeolite (framework Si/Al ratio of 2.4) was supplied by Linde, and γ-Al_2O_3 was supplied by Condea.

The Pt/zeolite catalysts were prepared by ion exchange of the HFAU and NaFAU zeolites using an adequate dilute solution of $Pt(NH_3)_4Cl_2$, continuously stirred for 4 h at room temperature. Afterward, the samples were filtered, washed, and dried overnight at 100 °C. Calcination was carried out at 300 °C for 6 h under dry air flow. The Pt/γ-Al_2O_3 sample was prepared by incipient wetness impregnation using an appropriate solution of H_2PtCl_6. The sample is then calcined at 500 °C for 2 h under dry air flow. The calcined samples were then tableted and crushed to 0.2- to 0.4-mm size. Before reaction the catalysts were reduced in situ under hydrogen flow at 300 °C for 2 h.

The dispersion of platinum (Table 1) was determined by the toluene hydrogenation reaction [20]. This reaction was carried out at 110 °C in a flow reactor at atmospheric pressure. To minimise the thermal effects of the reaction a *n*-hexane/toluene (5/1) mixture was used as feed. The molar ratio of hydrogen to the mixture *n*-hexane/toluene was equal to 45. The number of accessible atoms of platinum was determined by comparing the initial activity of the catalyst with the activities obtained with standard Pt/HFAU catalysts of known dispersion [20].

Table 1
Properties of the catalysts used

	% Pt	Dispersion (%)
Pt/HFAU	0.1	35
Pt/NaFAU	0.2	39
Pt/γ-Al_2O_3	0.3	51

2.2. Reaction study

The reactions were carried out in a fixed-bed reactor (BTRS Jr Autoclave Engineers) at atmospheric pressure (Fig. 1). The catalyst sample (0.140 g) was supported in a small plug of glass wool in a vertical stainless-steel tubular reactor. The reactor was inserted into an oven, and the temperature controlled by a Eurothem 847 controller with PID action. The temperature was measured by a K-type thermocouple that was inserted into the catalyst bed. The feed gas (20% O_2 in nitrogen (Air Liquide)) with a concentration of MIBK of 1340 ppmv or a concentration of *o*-xylene of 1500 ppmv was introduced in the reactor with a total flow rate of 4.16 mmol min^{-1}, which was controlled by mass-flow controllers (Bronkhorst). The desired concentration of MIBK or *o*-xylene was obtained by passing part of the feed gas through a saturator which was kept at the appropriate temperatures by means of a cryostatic bath (Techne). The space velocity was kept constant in all the experiments (20,000 h^{-1}, calculated at ambient temperature and pressure).

The analytical system consisted of a gas chromatograph (Tremetrics 9001) equipped with a flame ionisation detector (FID) for the analysis of the hydrocarbons, and two nondispersive infrared (NDIR) analysers for the analysis of CO (Analytical Development Company) and CO_2 (NOVA Analytical Systems Inc.). The GC was fitted with a CP Wax 52 capillary column, with 30 m and 0.32 mm of internal diameter, kept at 70 °C. The conversion into CO_2 is defined as the molar flow rate of CO_2 at the reactor outlet, divided by six (or eight) times the molar flow rate of MIBK (or *o*-xylene) in the feed.

The total amount of coke in the catalysts after reaction was measured by temperature-programmed oxidation in air (TPO). After reaction, the catalyst was cooled in nitrogen till 80 °C. Then a stream of air was passed and the temperature increased at 10 °C min^{-1} till 520 °C and was maintained until there was no further change in the gas concentration. The

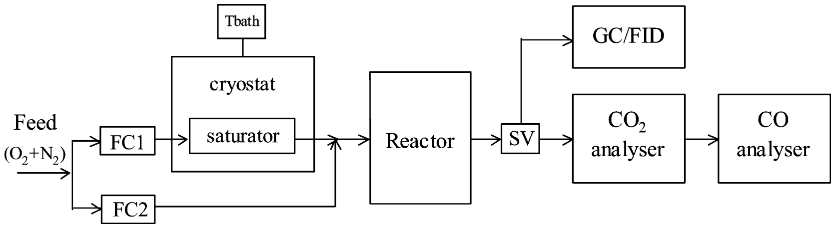


Fig. 1. Scheme of the experimental setup. FC1, FC2, mass-flow controllers; SV, sampling valve.

CO and CO_2 released were determined on-line by the NDIR analysers. The total amount of coke was calculated by integration of the CO and CO_2 curves obtained.

Temperature-programmed desorption was also carried out after certain runs. The catalysts were cooled in nitrogen till 100 °C after reaction and then the temperature was increased at 5 °C min^{-1} till 520 °C and was maintained until there was no more reactant at the exit. The effluent was analysed by GC/FID. Temperature-programmed desorption was also carried out after preadsorption of the reactants at 40 °C from a nitrogen stream, using the same concentration as in the reaction study. After saturation (when the concentration of reactant did not change), the catalyst was purged in a nitrogen stream and the TPD started.

The products of reaction that remained adsorbed in the catalysts were identified by GC/MS (Varian CP-3800 with a ITD Saturn 2000, column: CP-Sil 8 CB lowbleed/MS). After reaction, the catalysts were placed in a closed glass vessel filled with nitrogen. This vessel was then heated up to the temperature corresponding to the maximum of the reactive coke peak in the TPOs. A sample of the desorbed products was collected and analysed by GC/MS.

3. Results

3.1. Oxidation of MIBK

In a previous study [18] it was found that oscillations occurred in the apparent conversion of MIBK into CO_2 over a Pt/HFAU catalyst in a narrow temperature range. This phenomenon was directly related to the formation of easily oxidised compounds that remained inside the zeolite pores, which were detected by a peak at low temperatures in the TPO analysis. These compounds are referred to as “reactive coke”.

In order to investigate the nature of these compounds, TPD analysis of the reactant was performed after reaction at 180 °C. The TPD and TPO analyses are shown in Fig. 2. As already described in the earlier publication [18], the TPO shows two types of coke with different reactivities: one that oxidises at low temperature (reactive coke) and another that oxidises at higher temperature. The TPD of MIBK after reaction shows a broad peak with a maximum at 240 °C. This means that some MIBK remains adsorbed on the catalyst after reaction at 180 °C. The presence of MIBK adsorbed on the catalyst after reaction was also confirmed by GC/MS. Along with MIBK, several other low molecular weight compounds were detected in small amounts, like *i*-butene, branched heptenes, acetone, and propionic acid.

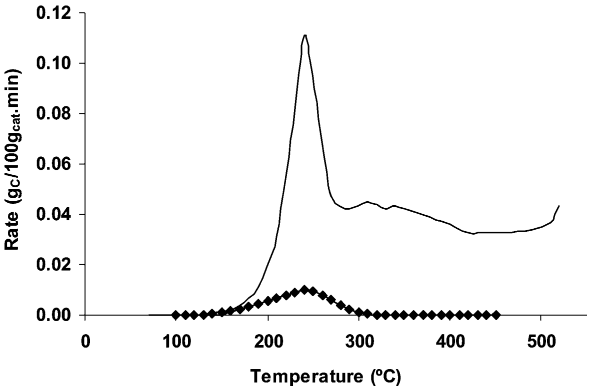


Fig. 2. TPO (—) and TPD of MIBK (⧫) after reaction of MIBK on the Pt/HFAU catalyst at 180 °C.

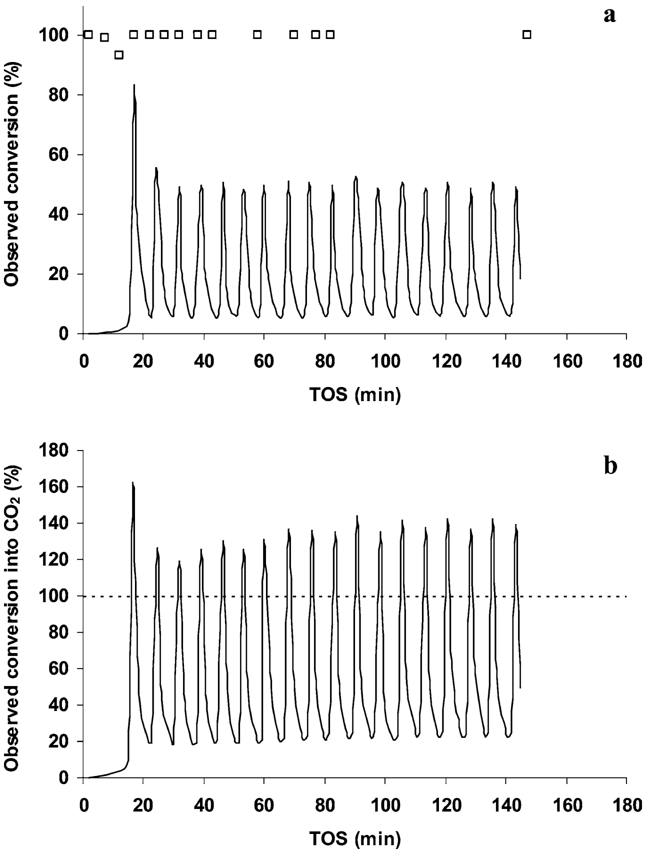


Fig. 3. (a) Total conversion of MIBK (☐) and apparent conversion into CO (—) and (b) apparent conversion into CO_2 on NaFAU zeolite at 250 °C.

The same phenomenon was also observed with the Pt/NaFAU; i.e., oscillations in the apparent conversion into CO_2 occurred between 180 and 200 °C. As in the case of the acidic catalyst, a more reactive type of coke was also observed in the TPO (peak maximum at 220 °C).

Surprisingly, the oscillation behaviour was also observed on the NaFAU zeolite at 250 °C. In this case, while the total conversion of MIBK was always close to 100%, not only the apparent conversion into CO_2 oscillated, but also the apparent conversion into CO (Fig. 3). In fact, this zeolite alone (without platinum) exhibited a high oxidation activity for the main reaction (MIBK oxidation) and a reasonable CO_2 selectivity (conversion into CO_2 higher than 60% at 300 °C). In the TPO after reaction at 220 °C, the onset temperature

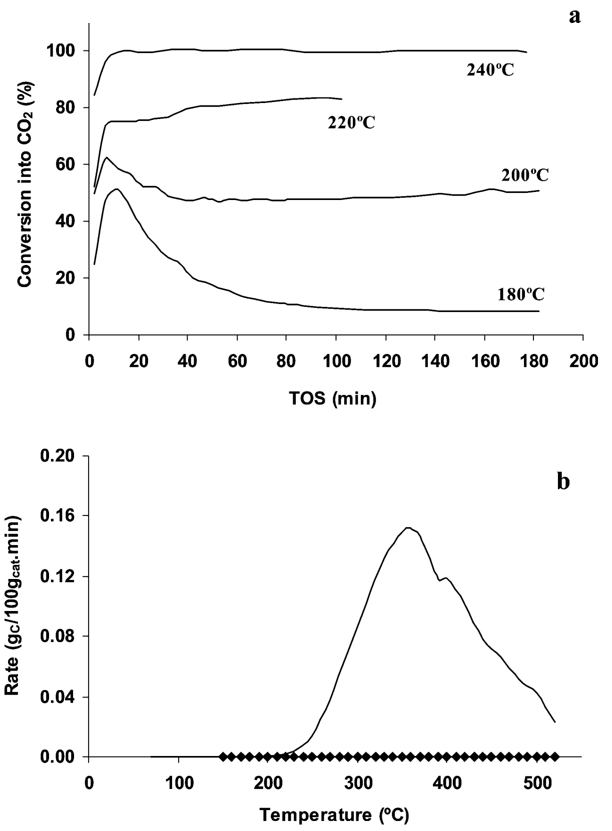


Fig. 4. (a) Influence of time on stream (TOS) on the conversion of MIBK into CO_2 on the $Pt/\gamma\text{-}Al_2O_3$ catalyst at 240, 220, 200, and 180 °C and (b) TPO (—) and TPD of MIBK (♦) after reaction at 180 °C.

was 240 °C and the first peak maximum was at 300 °C, so the reactive coke was again present. The TPD of MIBK after reaction at the same temperature showed also a large amount of this compound.

Whatever the reaction temperature, in the case of the oxidation over $Pt/\gamma\text{-}Al_2O_3$, no oscillations were observed (Fig. 4a). At 220 °C the catalyst reached a steady-state conversion into CO_2 of 85%, while on the other catalysts the oscillations occurred at temperatures just before the temperature for which the conversion of MIBK was complete. The TPO after reaction at 180 °C is presented in Fig. 4b together with the TPD of MIBK. In this case, the TPO presents only one peak (maximum at 360 °C), the onset temperature being 210 °C. Furthermore, the TPD of MIBK after reaction (Fig. 4b) shows only traces of MIBK still adsorbed on the catalyst.

It should be noted that the exothermic character of the oxidation reactions led to increases in the catalyst temperature. The exothermicity of the reactions could be measured by the thermocouple placed into the catalyst bed. When no oscillations were observed, the temperature increased after starting the reaction, reaching a constant value which remained constant till the end of the run. However, in the case of cyclic behaviour there were also temperature oscillations. These temperature oscillations were synchronised with the oscillations in the apparent conversion into CO_2.

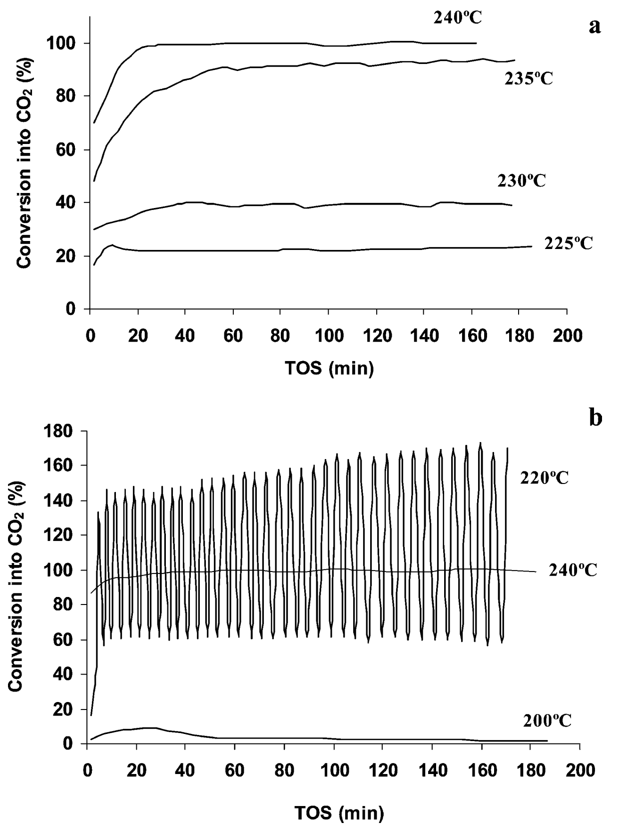


Fig. 5. Influence of time on stream (TOS) on the conversion of *o*-xylene into CO_2 on (a) the Pt/HFAU catalyst at 240, 235, 230, and 225 °C and (b) the Pt/NaFAU catalyst at 240, 220, and 200 °C.

3.2. *Oxidation of o-xylene*

The results of the conversion of *o*-xylene into CO_2 versus time on stream (TOS) obtained over Pt/HFAU and Pt/NaFAU catalysts are compared in Fig. 5 at different temperatures. In the temperature range studied, no oscillations occurred when the oxidation of *o*-xylene was tested with the Pt/HFAU catalyst (Fig. 5a).

However, with the Pt/NaFAU catalyst this phenomenon occurred again at 220 °C (Fig. 5b). At 240 °C the conversion into CO_2 is complete and no MIBK is present at the reactor exit. At 200 °C the conversion into CO_2 increases initially, decreasing afterward till a constant plateau at 3%. At 220 °C the apparent conversion into CO_2 oscillates between 60% and a value between 160 and 170%. Oscillations in the temperature of the catalyst bed ranging from +3 to +40 °C were also observed, which were synchronised with the oscillations in the conversion into CO_2.

The TPO/TPD of these samples after reaction at different temperatures are shown in Fig. 6. In the case of the reaction with the Pt/HFAU catalyst, the amount of the more reactive coke is not significant. The coke starts to oxidise at 170 °C and the rate increases till the end of the analysis. Moreover, there are only traces of *o*-xylene present on the TPD experiments, confirming that *o*-xylene did not stay adsorbed in the catalyst after reaction.

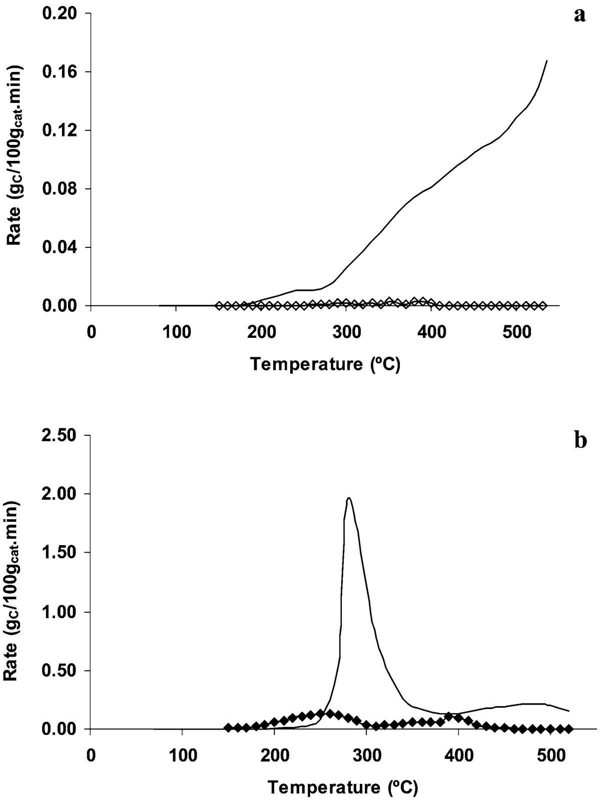


Fig. 6. TPO/TPD after reaction of *o*-xylene on (a) Pt/HFAU catalyst at 225 °C, TPO (—) and TPD of the reactant (◊), (b) Pt/NaFAU catalyst at 200 °C, TPO (—) and TPD of the reactant (◆).

On the other hand, with the Pt/NaFAU catalyst there is a first peak in the TPO, corresponding to the more reactive compounds which start to oxidise at 180 °C, presenting a maximum at 280 °C. There is also some *o*-xylene adsorbed after reaction, as can be seen in the TPD analysis (Fig. 6b).

The presence of xylene adsorbed on the catalyst after reaction was also confirmed by GC/MS. Along with *o*-xylene, there was also some toluene and trimethylbenzene. The same technique was also tested in the Pt/HFAU catalyst after reaction. Only traces of xylene were observed in this case.

4. Discussion

4.1. Oscillation mechanism

In a previous publication [18] it was shown that oscillations in the conversion of MIBK into CO_2 over a Pt/HFAU catalyst were directly related to the presence of a reactive type of coke on the catalyst, which was detected in the TPO experiments. This conclusion was based on TPO experiments performed after stopping the reaction at a maximum and a minimum of the oscillations. It was observed that the intensity of the peak of the more reactive coke was smaller when stopping the reaction at a maximum, which means that this type of coke was consumed in the process and therefore it was responsible for the oscillations. In the present study this phenomenon was investigated on different systems, namely on different catalysts and with two different VOCs, the main results being collected in Table 2.

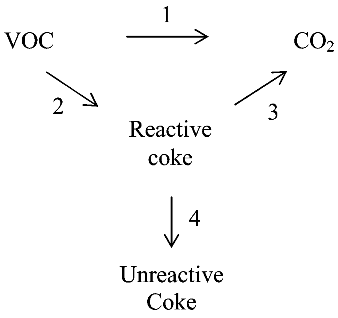
The experimental findings can be rationalised with the aid of the simplified reaction scheme (Scheme 1).

In the presence of the catalyst, the VOC can follow two reaction paths in parallel: total oxidation into CO_2 (and H_2O), and formation of reactive coke. The reactive coke can be further converted into unreactive coke (i.e., which cannot be oxidised at the temperatures used in the present study), or oxidised into CO_2 (and H_2O). In general, the coke formation reactions should occur on the acid or basic sites, while

Table 2
Summary of the results obtained

	Reaction		TPO		TPD*	
	Xylene	MIBK	Xylene	MIBK	Xylene	MIBK
Pt/HFAU47	$T_{100\%} = 240\,°C$ No oscillations	$T_{100\%} = 195\,°C$ $T_< = 185\,°C$ $T_> = 200\,°C$	$T_{onset} = 170\,°C$ $T_M = 520\,°C$	$T_{onset} = 170\,°C$ $T_{M1} = 240\,°C$ $T_{M2} = 520\,°C$	No	Yes
Pt/NaFAU	$T_{100\%} = 240\,°C$ $T_< = 200\,°C$ $T_> = 240\,°C$	$T_{100\%} = 200\,°C$ $T_< = 160\,°C$ $T_> = 220\,°C$	$T_{onset} = 180\,°C$ $T_{M1} = 280\,°C$ $T_{M2} = 470\,°C$	$T_{onset} = 160\,°C$ $T_{M1} = 220\,°C$ $T_{M2} = 450\,°C$	Yes	n.d.
Pt/Al_2O_3		$T_{100\%} = 240\,°C$ No oscillations		$T_{onset} = 210\,°C$ $T_M = 360\,°C$		No
NaFAU		$T_{100\%} = 250\,°C$ $T_< = 220\,°C$ $T_> = 270\,°C$		$T_{onset} = 240\,°C$ $T_{M1} = 300\,°C$ $T_{M2} = 400\,°C$		Yes

$T_{100\%}$: temperature above which the conversion of MIBK is complete.
$T_<$, $T_>$: temperature range where oscillations were observed (experiments carried out at 5 °C intervals on Pt/HFAU and 20 °C intervals otherwise).
T_{onset}: temperature above which the oxidation rate is higher than $10^{-5}\ g_C\ g_{cat}^{-1}\ min^{-1}$.
T_M: temperature of the maxima of the TPO peaks.
[*] Presence of reactant adsorbed on the catalyst after reaction.



Scheme 1.

the conversion into CO_2 (and H_2O) should occur on the oxidation sites.

Table 2 shows that there are oscillations whenever there is reactive coke in the TPO, as well as adsorbed VOC on the catalyst (as shown by TPD). These oscillations occur in a very narrow temperature range $]T_<, T_>[$ (Table 2). In these systems, at high temperatures (above $T_>$), r_1 and r_3 will be much higher than r_2; therefore, there is no accumulation of coke (reactive or unreactive), and the conversion into CO_2 will be complete. At low temperatures (below $T_<$), r_3 is negligible (as shown in the TPOs) and both types of coke will be present in the catalyst. In these two cases there are no oscillations, either in the temperature or in the apparent conversion into CO_2.

At intermediate temperatures, r_2 will be higher than r_3 initially, but r_3 is not negligible; reactive coke is formed faster than it is oxidised, and starts to accumulate, together with unreactive coke. However, as a result of the exothermic oxidation reaction 3, there will be a local temperature rise of the catalytic bed which leads to the self-heating of the catalyst. As the temperature increases, r_3 increases faster than r_2. A situation will be reached where r_3 will be higher than r_2, and most of the accumulated reactive coke will be consumed. Then, there will be no extra heat released, the temperature will drop to the baseline, and a new cycle starts. This mechanism explains the observed behaviour of the oscillation in the apparent conversion into CO_2 and in the temperature, provided that the activation energy for reactive coke combustion is higher than the activation energy for reactive coke formation ($E_3 > E_2$).

In the systems where no oscillations were observed, neither reactive coke in the TPO nor adsorbed VOC in the TPD were present (Table 2). In these cases, the rate of reaction 2 will never be higher that the rate of reactions 3 and/or 4 at any temperature, because no reactive coke is present after reaction. At high temperatures r_1 will be higher than r_2 and all the VOC will be converted into CO_2. At low and intermediate temperatures, r_2 cannot be neglected and there will be coke formation. However, r_3 is negligible and there will be only unreactive coke. In these cases, it can be concluded that the phenomenon does not occur because there is no accumulation of oxidisable compounds that can lead to the oscillations.

Table 3
Amount of reactive coke and adsorbed VOC present in the catalyst after reaction at specific temperatures

VOC	Catalyst	Reaction temperature (°C)	Reactive coke[a] ($g_C/100\ g_{cat}$)	Adsorbed VOC[b] ($g_C/100\ g_{cat}$)
MIBK	Pt/HFAU	180	0.5	0.2
MIBK	NaFAU	220	3.0	2.0
o-Xylene	Pt/NaFAU	200	8.1	3.8

[a] Determined by integration of the first peak of the TPOs, after deconvolution.

[b] Determined by integration of the TPDs after reaction, expressed as carbon.

We can now discuss the nature of the reactive coke and why it is formed only in some catalysts from the VOC molecules studied.

4.2. *Nature of the reactive coke*

From the TPD experiments after reaction, it is clear that the presence of the reactive coke in the TPO is associated with the presence of reactant which remains adsorbed on the catalyst after reaction. In the case of the oxidation of MIBK, adsorbed reactant was detected in the Pt/HFAU catalyst and in the NaFAU zeolite after reaction, while only traces were detected in the Pt/γ-Al_2O_3 catalyst. With *o*-xylene, a large amount of reactant was detected after reaction on Pt/NaFAU, while only traces were found on Pt/HFAU. So, the systems where adsorbed reactant was detected after reaction are precisely those where a reactive coke is found in TPO (cf. Table 2). Therefore, part of the first TPO peak is certainly due to the oxidation of adsorbed reactant. The amount of reactant present in the catalysts after reaction is shown in Table 3, together with the amount of reactive coke after reaction. It is clear that an important amount of the reactive coke is in fact adsorbed reactant. The GC/MS analysis shows that other compounds formed during the reaction are also desorbed at the temperature of the maximum of the TPOs, suggesting that these compounds are also part of what we call reactive coke.

In order to determine the adsorption strength of the catalysts, temperature-programmed desorption experiments were made with both VOCs, preadsorbed at 40 °C (Fig. 7). In the case of MIBK (Fig. 7a), there is a large difference in the adsorption strength when sodium cations are present. In this case, the desorption of MIBK starts at 200 °C and presents a broad peak with a maximum at around 360 °C. With the Pt/γ-Al_2O_3 catalyst, MIBK desorbs at much lower temperatures, with a peak maximum at 130 °C. It should be noted that at 190 °C the desorption rate is very low ($8 \times 10^{-5}\ g_C\ g_{cat}^{-1}\ min^{-1}$) and only traces of MIBK are found at higher temperatures. With the Pt/HFAU catalyst, MIBK also desorbs at low temperatures (peak maximum at 130 °C), but at 190 °C there is still some MIBK adsorbed, the desorption rate of MIBK being close to zero only at 320 °C.

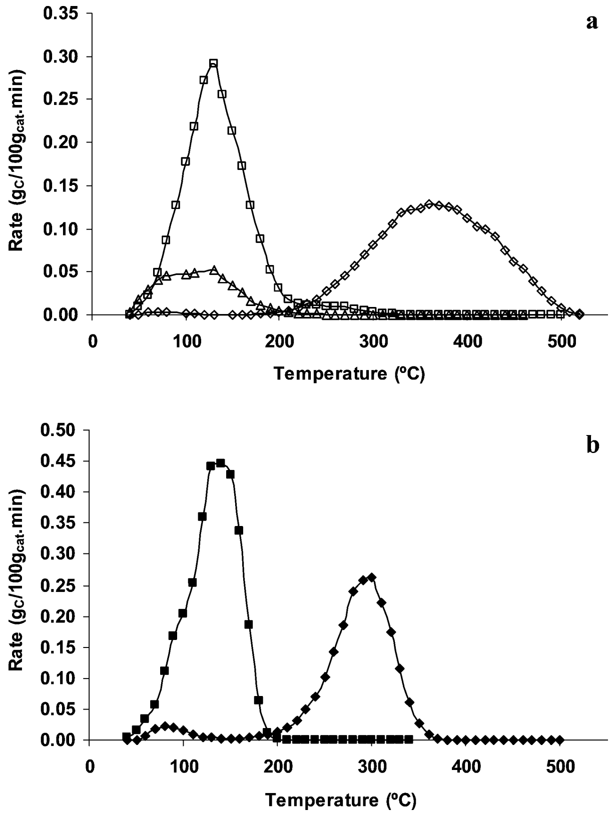


Fig. 7. TPD after preadsorption at 40 °C of: (a) MIBK over Pt/HFAU (□), Pt/γ-Al_2O_3 (△), and NaFAU (◇) catalysts; (b) *o*-xylene over Pt/HFAU (■) and Pt/NaFAU (◆) catalysts.

The interaction of acetone with ZSM-5 zeolites at ambient temperature was studied by FTIR spectroscopy by Kubelková et al. [21]. They found that acetone adsorbs on the acidic zeolite (HZSM-5) via the bridging hydroxyls and that the C=O bond in ketones is more perturbed by these bridging hydroxyls than by the electron-accepting sites (NaZSM-5 and dehydroxylated HZSM-5); so, there is a higher shift in the C=O IR band in the acidic zeolite. Panov and Fripiat [22] also describe Lewis acid sites binding acetone less energetically than Brønsted acid sites, when studying the acetone condensation reaction with several zeolites and alumina.

In the present work, it was shown (Fig. 7a) that MIBK is less adsorbed in the Pt/γ-Al_2O_3 catalyst (with only Lewis acid sites) than in the Pt/HFAU catalyst (with Brønsted and Lewis acid sites), which is in agreement with the cited references. Therefore, adsorption on the Lewis acid sites of the γ-Al_2O_3 is not so strong as in the HFAU zeolite. On the other hand, MIBK adsorbed on the NaFAU zeolite desorbs at higher temperatures when compared to the acidic catalysts. This means that, in this case, MIBK is more strongly adsorbed on the cation sites of the zeolite than on the acidic sites. Nevertheless, it is clear that some MIBK remains adsorbed at temperatures higher than the reaction temperatures on both catalysts (Pt/HFAU and NaFAU) and that this does not happen with Pt/γ-Al_2O_3.

In the case of *o*-xylene (Fig. 7b), it is also clear that the basic catalyst is able to keep the reactant adsorbed up to higher temperatures. *o*-Xylene starts to desorb at 170 °C and presents a peak maximum at 300 °C. On the contrary, desorption takes place at much lower temperatures with the Pt/HFAU catalyst: the reactant starts to desorb near 50 °C and the peak maximum is at 140 °C. It should be noted that no *o*-xylene remains adsorbed in the catalyst at 210 °C and higher temperatures.

It is well know that cations in zeolites are adsorption sites for molecules with π electrons [23]. Benzene, for example, is used to characterise the location of cations in zeolites [24]. In faujasite, benzene can adsorb on the cation or on the oxygen atoms of the 12R window. In the case of C8 aromatics the interactions are only with the cations [25], and are governed by a balance between the aromatic basicity and the Lewis acid character of the cation on the zeolite [25].

From the TPD experiments, we can conclude that the adsorption of xylene and MIBK on the cations of the faujasite is much stronger than in the acidic zeolite. The adsorption strength of the support is directly related to the oscillatory behaviour in the apparent conversion into CO_2. When the catalyst is not able to retain the VOC molecule adsorbed up to temperatures higher than the reaction temperature (like Pt/γ-Al_2O_3 with MIBK and Pt/HFAU with *o*-xylene), oscillations cannot occur because there are no oxidisable compounds accumulated in the catalyst. In the other cases, oscillations occur as a consequence of the accumulation of adsorbed compounds (reactant and other molecules that are produced from it and that do not desorb, which are the reactive coke) that can oxidise at a sufficiently high rate to cause a significant increase in the catalyst temperature, leading to cyclic oscillations in the apparent conversion into CO_2.

It is then clear that the oscillatory phenomenon is mainly determined by the adsorption properties of the support. In particular, a support that is capable of adsorbing the reactant (and other easily oxidisable compounds) at temperatures higher than the reaction temperature can originate oscillations in the conversion into CO_2 when the reaction temperature is close to the temperature corresponding to complete conversion.

5. Conclusions

- Oscillations in the apparent conversion into CO_2 occur in the catalytic oxidation of MIBK and *o*-xylene whenever there is the presence of reactive coke in the TPOs. In these systems, at intermediate temperatures, reactive coke is formed faster than it is oxidised and starts to accumulate. The oxidation of these compounds into CO_2 occurs at a sufficiently high rate to lead to the self-heating of the catalyst and to oscillations in the apparent conversion into CO_2.
- TPD of the reactant and GC/MS analysis after reaction show that the reactive coke is composed of reactant and

other low molecular weight compounds that remain adsorbed in the catalyst.
- The occurrence of oscillations is determined by the adsorption properties of the support; in particular, a support that is capable of adsorbing the reactant at temperatures higher than the reaction temperature can originate oscillations in the apparent conversion into CO_2.

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