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New Hypotheses on the Mechanism of the Deterioration of Cordierite Diesel Filters in the Presence of Metal Oxides

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Abstract: It is well known that the durability of the honeycomb structures made of cordierite, used as filters for diesel exhaust emissions, is affected by some components of the soot which can react with cordierite during regeneration cycles at high temperature (up to 1000°C). Amongst all the components of the soot, sodium is particularly dangerous because of its destructive effect on the cordierite structure.

The interaction between sodium carbonate and cordierite has been studied by means of FTIR spectroscopy and the following statements can be made: even if very slowly, the attack on cordierite has already begun at 500°C and proceeds very quickly onwards from 600°C; an amorphous phase is formed at 700°C; at higher temperature, the amorphous phase crystallizes releasing sodium which, during cooling, reacts with carbon dioxide, yielding again sodium carbonate; this carbonate will act as sodium source in the following thermal regeneration cycles. During this study it has also been shown that the first attack is not determined by the sodium ion diffusion into the pseudo-zeolitic channels of the cordierite lattice.

INTRODUCTION

In previous papers[1-3] the interaction of some oxides present in the soot transported by the diesel exhaust gases with the cordierite filter, above all during the filter regeneration cycles at high temperature, up to 1000°C, was investigated. The primary role of sodium in destroying the cordierite structure was also underlined.[3]

Starting from XRD data, SEM observations and dilatometric measurements, an attempt was made[2,3] to explain this phenomenon: it seemed that Na^+ etched cordierite structure also profiting by the presence of zeolite-type channels into which it could easily and deeply diffuse. In addition, it was also demonstrated[1,2] that a local concentration of small quantities of sodium yielded sodium magnesium silicates and aluminosilicates: these compounds having a thermal expansion coefficient much higher than the cordierite one induced extended microcracks in the filters calcined at 1000°C.

Additional information was obtained from infrared spectroscopy, which confirmed the XRD data;[2] amorphous phases formed after a progressive increase of AlO_4 tetrahedra distortion in cordierite.

However, the almost constant band at 770 cm^{-1} imputed to the vibration of six tetrahedra rings[4] did not agree with the hypothesis of Na^+ diffusion into the zeolitic channels formed by them.

In addition, the presence of typical sodium carbonate bands in the IR spectra of the cordierite–sodium carbonate mixtures calcined at 1000°C for long times was puzzling when the presence of carbonate was not confirmed by XRD analysis.

Therefore, in this paper the results of the previous work are compared to the information obtained from FTIR investigation and an improved hypothesis concerning the mechanism of sodium interaction with cordierite during the filter lifetime is proposed.

EXPERIMENTAL

The samples investigated (Table 1) were:

- sodium carbonate (Carlo Erba PPR) (**a**);
- cordierite Baikowski (**b**);
- a mixture of (**a**) and (**b**) (1 : 1 by weight), before (**c**) and after (**c1–c13**) heat treatments.

The mixture was obtained by dry milling in a TZP ball mill.

The samples for heat treatment were bars obtained by uniaxial compaction of the powder at 400 MPa.

Heat treatments were carried out using a heating and cooling rate of 10°C/min and maintaining a plateau at the higher temperature for a fixed time; the cycles were performed in air or in nitrogen flow (200 ml/min); see Table 1. After the thermal cycles, the bars were crushed to a powder having a particle size lower than 40 μm.

In order to investigate the influence of ageing time on sodium carbonate reappearance after reaction with cordierite, samples **c1**, **c3**, **c4**, **c5**, **c6**, **c7** and **c13** were analyzed after an ageing time of about one year; on the other hand, samples **a**, **b**, **c**, **c2**, **c8**, **c9**, **c10**, **c11** and **c12** were analyzed immediately after preparation or after an ageing time as shown in Table 1.

FTIR analysis was performed on KBr pellets by Nicolet Magna-IR 550 spectrometer controlled by Omnic system, in the spectral range between 4000 and 300 cm^{-1}, with a minimum precision of ± 0·4 and average of ± 0·2 cm^{-1}. After noise removal, all the interferograms were expressed as absorbance spectra in order to automatically correct the baseline and, if necessary, to perform the automatic deconvolution. Subsequently, all the spectra were converted into percent transmittance. The wavenumbers presented have been reduced to unity. For the sake of easy graphic representation, only the more significant parts of the spectra, between 1800 and 300 cm^{-1}, are reported in the figures.

Table 1. Samples investigated by FTIR to study the interaction of Na$^+$ with cordierite as a function of thermal treatment conditions and ageing time

Samples	Thermal treatment conditions				Analysis after ageing time
	Comp.	Environm.	Maximum temp. (°C)	Time at T_{max}	
a	Na_2CO_3	—	—	—	0
b	Cordierite	—	—	—	0
c	Mixture	—	—	—	0
c1	Mixture	Air	500	5 min	1 year
c2	Mixture	Air	500	1 h	0
c3	Mixture	Air	600	5 min	1 year
c4	Mixture	Air	700	5 min	1 year
c5	Mixture	Air	800	5 min	1 year
c6	Mixture	Air	900	5 min	1 year
c7	Mixture	Air	1000	5 min	1 year
c8	Mixture	Air	1000	1 h	0
c9	Mixture	Air	1000	1 h	7 days
c10	Mixture	Nitrogen	1000	7 h	0
c11	Mixture	Nitrogen	1000	1 h	3 h
c12	Mixture	Nitrogen	1000	1 h	7 days
c13	Mixture	Air	1000	50 h	1 year

RESULTS AND DISCUSSION

The spectra of sodium carbonate (**a**), cordierite (**b**) and of their mixture thermally untreated (**c**) are presented in Fig. 1.

Spectrum **a** shows that sodium carbonate also contains the decahydrate form (typical single sharp bands at 1411, 902, 867, 686 cm^{-1}; a large and broad shoulder between 1750 and 1600 cm^{-1} and a shoulder at 850 cm^{-1}).

Spectrum **b** confirms the XRD data:[2] cordierite Baikowski is indialite (characteristic doublet shoulder at 1105 and 1085 cm^{-1}) and also shows that cordierite has absorbed significant quantities of moisture (large and broad band at 1640 cm^{-1}).

From spectrum **c**, it is possible to deduce that during mixing in a ball mill some perturbation of carbonate lattice and an increase of moisture adsorbed on the powders took place.

The spectra which enable one to follow the sodium attack as a function of temperature (**c1**, **c3**, **c4**, **c5**, **c6** and **c7**) and time (**c1**, **c2**, **c7** and **c13**) of heat treatment of the mixtures are collected in Fig. 2. If we compare spectra **c** and **c1**, it seems that calcination at 500°C for 5 min is able to reduce the $Na_2CO_3.10H_2O$ amount substantially in

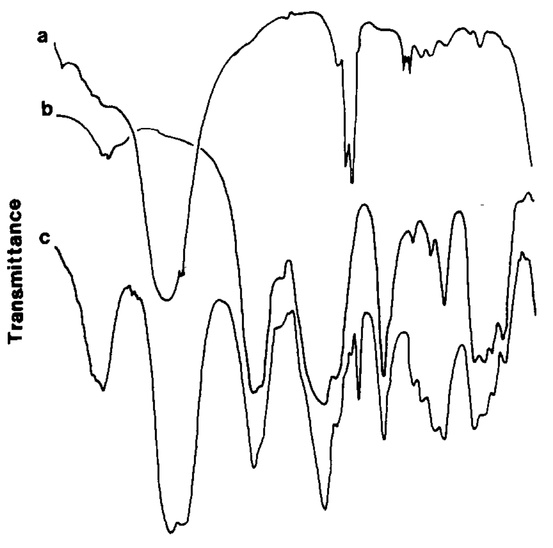

Fig. 1. FTIR spectra of (**a**) sodium carbonate, (**b**) cordierite Baikowski and (**c**) their mixture, 1 : 1 by weight.

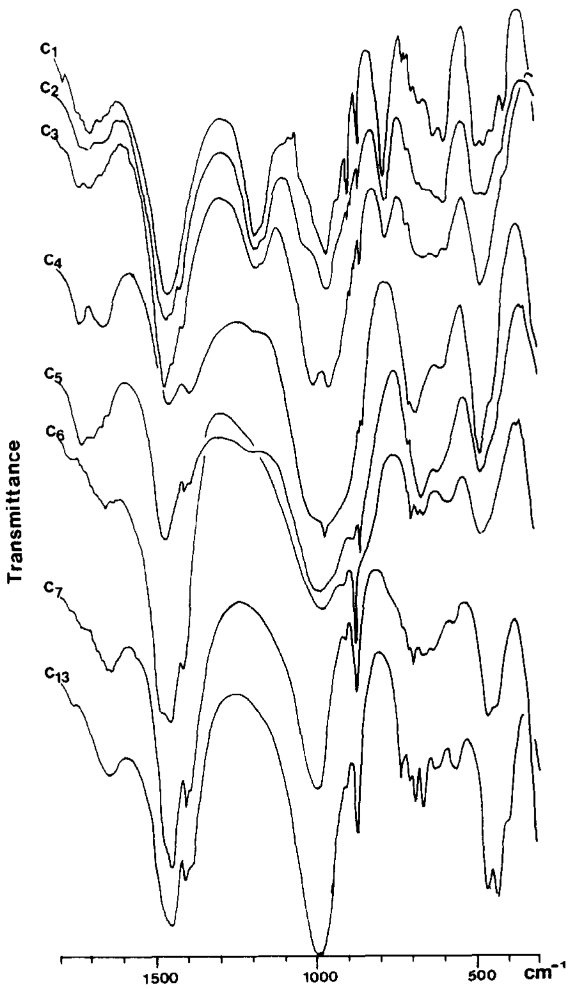

Fig. 2. FTIR spectra of the mixture calcined : (**cl**) at 500°C for 5 min; (**c2**) at 500°C for 1 h; (**c3**) at 600°C for 5 min; (**c4**) at 700°C for 5 min; (**c5**) at 800°C for 5 min; (**c6**) at 900°C for 5 min; (**c7**) at 1000°C for 5 min and (**c13**) at 1000°C for 50 h.

favour of Na_2CO_3 but not to start the reaction between cordierite and sodium carbonate. However, the reaction takes place after a longer heat treatment (see spectrum **c2**). For this reason, the spectra **c** and **cl**, after automatic deconvolution (labelled **c'** and **cl'**, respectively), are compared in Fig. 3 : in this way, it is possible to discover differences other than the simple conversion of the decahydrate carbonate into the anhydrous form.

In fact, no changes of the positions and intensities of the single sharp bands imputed to the SiO_4 asymmetric stretching bands (1265, 1229, 1185, 1146 and 1099 cm^{-1}) and to the six tetrahedra ring vibration (772 cm^{-1}) are detected, but a shift of the position and relative intensity of the single bands due to the AlO_4 asymmetric stretching was observed.

The more obvious changes shown in the spectral regions between 905 and 800 cm^{-1} and between 740 and 440 cm^{-1} cannot be considered, because of the carbonate contribution. Nevertheless the single sharp bands not influenced by bending of the CO_3 groups change from 1078, 1031, 992, 957 and 910 cm^{-1} (spectrum **c'**) to 1080, 1031, 996, 959 and 918 cm^{-1} (spectrum **cl'**), respectively, while the intensities of the bands reduce proportionally to the amplitude of their shift. From spectrum **c2** it clearly appears that the reaction between sodium and cordierite proceeds and a new phase forms.

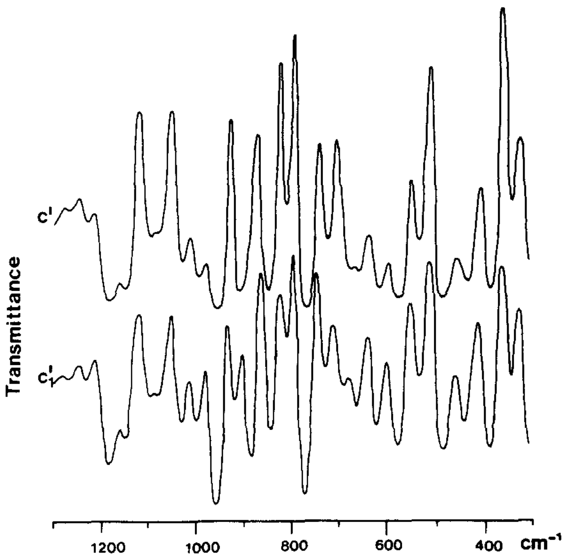

Fig. 3. Curves of automatic deconvolution of the FTIR spectra of the mixture calcined at 500°C (c') for 5 min and (cl') for 1 h.

In addition, after deconvolution, a very limited shift of some single sharp bands due to the cordierite SiO_4 groups (from 1265, 1229, 1185, 1146 and 1099 cm^{-1} to 1266, 1228, 1185, 1146 and 1098 cm^{-1}, respectively) and a small change of their relative intensities were detected; no perturbation of the single bands imputed to the six tetrahedra rings vibration was observed. It is possible to conclude that the reaction between sodium carbonate and cordierite has already begun at 500°C.

The SiO_4 tetrahedra are mostly located on the hexagonal rings and the asymmetric stretching bands of these groups and the vibration bands of the rings are little affected or not influenced at all by the modifications induced by the attack: these statements strongly support the hypothesis that the attack on cordierite starts from the surface, particularly from superficial aluminium and, perhaps, magnesium, rather than from the Na^+ diffusion inside the zeolitic channels.[2,3] It is not possible to be dogmatic about the attack from superficial magnesium because of the partial overlap between the MgO_6 group band (under 480 cm^{-1})[5] and the asymmetric bending of SiO_4 groups: however, the evolution of spectra **cl**, **c2** and **c3** in this region is clear.

In spectrum **c3** of the mixture treated at 600°C (Fig. 2), the asymmetric stretching bands of SiO_4

groups (1180 cm^{-1}) and the vibration bands of the cordierite rings (771 cm^{-1}) are still well identified but their intensity is markedly reduced because of the sodium attack on cordierite. In addition, a new phase already detected in spectrum **c2** is present. This phase cannot be identified by FTIR, because its bands overlap partially with those of residual cordierite and sodium carbonate; XRD analysis showed the presence of $Na_2Al_2SiO_6$.[2]

The spectrum **c4** in Fig. 2 clearly shows that at 700°C the cordierite is almost completely destroyed. In fact, a broadened shoulder at about 1180 cm^{-1} is the only signal ascribable to cordierite in this spectrum. The sample is highly disordered and the spectrum between 1300 and 300 cm^{-1} is typical of an amorphous material formed of sodium silicoaluminates.[6,7] In addition, the splitting and the increase of the broadening of the band between 1750 and 1600 cm^{-1} seems to be due to trapping of moisture into the amorphous phase.[7-10]

On the other hand, the splitting and the noticeable increase of broadening of the band at about 1450 cm^{-1} can be easily justified as due to the presence of CO_3 groups co-ordinated on metals of the amorphous structure[11] rather than to sodium carbonate, even if the presence of small quantities of the carbonate is supported by the two single sharp bands at 867 and 703 cm^{-1} and by XRD analysis.[2] The sudden formation of a large amount of amorphous phase may be probably imputed to an earlier melting of sodium carbonate (pure sodium carbonate melts at 851°C) due to the interaction with cordierite.

The spectrum **c5** in Fig. 2 shows that also after heat treatment at 800°C the amorphous phase is prevalent: however a certain reorganization of the silicoaluminate matrix near to the reappearance of small quantities of sodium carbonate during cooling is evident.

The heat treatment at 900°C (spectrum **c6**) does not show significant differences except a more evident appearance of sodium carbonate.

Moreover, spectra **c7** and **c13** show that also at 1000°C a long heat treatment (50 h) is necessary for reaching a sufficient crystallizaton of $Na_4Mg_2Si_3O_{10}$ (bands at 986, 735, 464 and 433 cm^{-1}); less evident is the appearance of crystalline $NaAlO_2$ (bands at 667, 624 and 564 cm^{-1}), detected by XRD.[2] The presence of sodium carbonate bands (see especially spectrum **c13**) is puzzling. In fact, after heat treatment sodium carbonate should be decomposed and most CO_2 should be removed from the sample.

Carbon dioxide, in fact, is partially soluble in fused compositions of the Na_2O–SiO_2 system[12] but, even supposing that all the sample was fused at 1000°C and the furnace atmosphere was pure CO_2, the maximum CO_2 molar soluble quantity should be about one-fifth of the Na_2O moles present in the sample. In the operating conditions adopted, only a small part of the sample is fused and the furnace atmosphere is air; so, the experiments were carried out in conditions which do not allow CO_2 to remain on the sample. It is reasonable to assume that sodium carbonate present in samples calcined at 1000°C is due to a subsequent reaction between the solid and atmospheric CO_2. For better understanding of this effect, the spectra of samples **c8**, **c9**, **c10**, **c11** and **c12** were recorded and reported in Fig. 4.

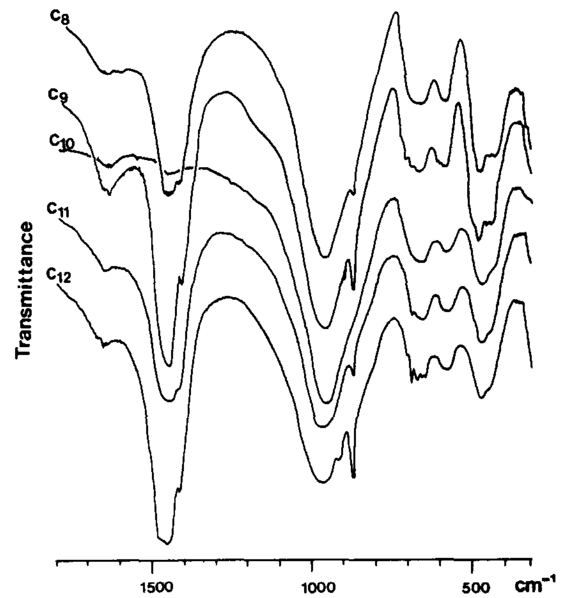

Fig. 4. FTIR spectra of the mixture calcined for 1 h at 1000°C: (**c8**) in air and recorded immediately; (**c9**) in air and recorded after 7 days in air; (**c10**) in nitrogen and recorded immediately; (**c11**) in nitrogen and recorded after 3 h in air and (**c12**) in nitrogen and recorded after 7 days in air.

As shown in spectrum **c8**, when calcining the sample in air, carbonate is still present at the end of the thermal cycle but increases again during the following seven days of ageing in air (spectrum **c9**).

On the other hand, spectrum **c10** of the above mixture calcined under nitrogen flow does not show the bands typical of sodium carbonate, but air exposure of the sample for 3 h (spectrum **c11**) is certainly enough to yield carbonate. After seven days the carbonate amount is comparable to that in the mixture calcined in air.

Sodium carbonate totally decomposes at 1000°C; but it is also clear that the phases crystallized during heat treatment must be full of active sites on sodium able to bind atmospheric CO_2 and to yield again carbonate. Such a reaction should stop very quickly owing to the saturation of surface sites unless the mechanism is similar to that of rust formation. In this case, however, increasing the carbonate amount, the short-range disorder of the other phases should also increase. This phenomenon probably occurs as shown in Fig. 4, where on increasing the carbonate amount the broadening of the bands of the non-carbonatic phases increases.

From the increase of the sodium carbonate bands in the spectra of Fig. 2, it can be concluded that the amorphous phase binds sodium so that the conversion to carbonate is prevented or slowed down. In fact, in spectrum **c4**, the highest amount of amorphous phase is coupled to the lower carbonate quantity.

CONCLUSIONS

From these data the following statements can be made:

— the attack of sodium on cordierite starts at 500°C and proceeds even more quickly at higher temperatures (600–700°C);

— this attack generates an amorphous phase in which sodium is strongly bound;

— when the temperature increases, the amorphous phase progressively crystallizes releasing part of the sodium in the form of sodium carbonate;

— the attack leads to the distortion of AlO_4 tetrahedra of cordierite structure, but neither the SiO_4 tetrahedra nor the six tetrahedra rings are affected;

— consequently, the mechanism of the first deterioration of cordierite cannot be imputed to the Na^+ diffusion into the pseudo-zeolitic channels of the cordierite structure.

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