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Thermal Stability of Cordierite Catalyst Supports Contaminated by Fe_2O_3, ZnO and V_2O_5

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Abstract

The effect of pollution of diesel particulate filters on their thermal and chemical stability has been studied. Commercial cordierite supports were contaminated, separately, by Fe_2O_3, ZnO and V_2O_5, and their evolution after thermal treatment in the range 800°C to 1200°C was followed by XRD and SEM.

The presence of Fe_2O_3 had little effect, whereas V_2O_5 reacted completely even at the lowest studied temperature, giving crystalline silica and aluminium and magnesium vanadates; the formation of a zinc silicate, a zinc aluminate with spinel structure and a glassy phase was observed above 1000°C in ZnO-contaminated samples. The differences in reactivity and nature of the reaction products were explained taking into account the low melting point of V_2O_5 and its acidic character. The microstructural changes were correlated with the mechanical properties of the supports.

Der Effekt der Verschmutzung von Dieselpartikelfiltern auf ihre thermische und chemische Stabilitat wurde untersucht. Kommerzielle Kordierittrager wurden jeweils mit Fe_2O_3, ZnO und V_2O_5 kontaminiert, und ihre Entwicklung nach einer Warmebehandlung im Bereich zwischen 800 und 1200°C mittels XRD und SEM untersucht.

Fe_2O_3 zeigte nur einen geringen Effekt, wahrend V_2O_5 auch bei den niedrigsten untersuchten Temperaturen vollstandig reagierte, wobei sich kristallines Silikat, Aluminium und Magnesiumvanadate bildeten. In mit ZnO verunreinigten Proben bildete sich oberhalb von 1000°C Zinksilikat, ein Zinkaluminat mit einer Spinellstruktur und eine Glasphase. Die unterschiedlichen Reaktionen lassen sich auf den niedrigen Schmelzpunkt von V_2O_5 und seinen saueren Charakters zuruckfuhren. Die Veranderungen im Gefuge wurden mit den mechanischen Eigenschaften des Tragers korreliert.

Concernant des filtres de particules émises par le diesel, a été étudié l'effet de la pollution sur leur stabilité thermique et chimique. Des supports de cordierite commercials ont été contaminés séparément, par Fe_2O_3, ZnO et V_2O_5, et leur évolution après traitement thermique a temperature comprise entre 800°C et 1200°C a été suivie par le XRD at SEM.

La présence de Fe_2O_3 a peu d'effet, par contre V_2O_5 reagit completement a partir des plus basses temperatures étudiées, donnant de la silica crystalline et des vanadates de magnesium et aluminium, la formation du silicate de zinc, de l'aluminate de zinc à structure spinelle et une phase vitreuse a été observée au dessus de 1000°C dans les échantillons contaminés au ZnO. Les différences concernant la réactivité et la nature des produits de la réaction ont été expliquées prenant en compte le point de fusion de V_2O_5 et son caractère acidique. Les changements microstructurals ont été liés aux propriétés mécaniques des supports.

1 Introduction

Cordierite materials are widely studied for a number of technological applications as different as buffer layers in microelectronics[1,2] and diesel particulate filters.[3] Apart from the low electrical conductivity, the most interesting properties, regarding the application in the automotive industry, lie in the low thermal expansion coefficient, high thermal shock resistance and good thermal stability up to 1460°C, together with the low cost of raw materials and easy molding. For these reasons cordierite filters with honeycomb shaped structures for engine exhaust filtration are nowadays components that are of interest for millions of cars, and engines in general.

During service, the stability of a cordierite filter is threatened by thermal gradients and temperatures that can be locally as high as 1100°C due to regeneration and to the temperature of the exhaust gas.[4] Previous work by the authors[5] showed that the pollutants emitted from the engine, at the regeneration temperature, can affect severely the microstructure and properties of cordierite. In particular, it was shown that the presence of calcium oxide and sodium oxide led to the decomposition of a surface layer of cordierite, with the formation of several compounds. Silicates with similar structures were observed to form $2CaO\,2Al_2O_3{-}4SiO_2$ and $2Na_2O{-}2Al_2O_3{-}4SiO_2$ for Na_2O and CaO contaminated samples, respectively. Moreover, a thick glaze made of a glassy phase and spinel formed in the presence of sodium at 1200°C. The formation of these phases had a marked influence on the mechanical properties of the supports, mainly because of the thermal expansion mismatch between the transformed surface layer and the bulk.[6,7]

In the present paper, the effect of pollution by the oxides of three metals present in the engine exhaust gas on cordierite supports was considered: Zn from the oil, Fe from the engine abrasion and from the fuel (combustion additive) and V, present in the catalytic compounds and in many petroleum fuels. Recently papers have been published[8,9] concerning hot corrosion of alumina and stabilized zirconia coatings by V_2O_5 in the temperature range 700–900°C. Samples contaminated with Fe_2O_3, ZnO and V_2O_5 were thermally treated, and the evolution of the microstructure was studied by SEM and XRD.

2 Experimental

Samples of porous cordierite were cut from diesel particulate filters (Corning EX 66 100/25). As shown by the chemical composition (Table 1), as received supports contained a considerable fraction of impurities together with MgO, Al_2O_3 and SiO_2.

Table 1. Chemical composition of original supports (standard deviation in parentheses)

Oxide	*Weight percentage*
MgO	13.42 (0.2)
Al_2O_3	35.20 (0.2)
SiO_2	49.42 (0.2)
CaO	0.31 (0.02)
TiO_2	0.42 (0.02)
Na_2O	0.41 (0.02)
K_2O	0.15 (0.04)
Fe_2O_3	0.67 (0.04)

Three sets of samples were contaminated with iron, vanadium and zinc oxides. The contamination was realized by dipping samples into solutions of the appropriate concentration of soluble compounds of each metal and calcining the dehydration precipitates. The amounts of pollutant were suggested by the chemical analysis of a catalytic trap used for 100 000 km on a diesel engine.[10]

The concentration of each solution was such to obtain the desired percentage of pollutant. To have 3.0 wt% Fe in the form of Fe_2O_3, after dipping in $FeCl_3$ solution, samples were slowly dehydrated (48 h at 30°C) and then calcined for 3 h at 400°C. The same procedure was followed for ZnO contamination (3.0 wt% Zn in the form of ZnO), using a $Zn(NO_3)_2$ solution and calcining at 450°C.

The procedure was more complex for vanadium oxide contamination because of the low solubility of vanadium pentoxide in water (0.070 g/liter). Samples were dipped for 5 h in a 100 ml solution containing 5 g V_2O_5; the pH was raised to 9 by addition of ammonium hydroxide to obtain the deposition of ammonium metavanadate (NH_4VO_3) on the support. After that, samples were dehydrated (48 h at 30°C) and calcined (3 h at 350°C). In order to have 2 wt% of V in the form of V_2O_5, the procedure was repeated several times. Both the original and the contaminated samples were treated for 3 h at 800°C, 1000°C and 1200°C in air. The length of thermal treatment was established according to the number and length of regeneration cycles sustained during the exercise;[10] however, it must be considered that the regeneration cycle is discontinuous (length ~ 1 min), whereas the present treatments were isothermal and continuous.

XRD experiments were conducted through a Rigaku instrument, using CuK_α radiation produced at 40 kV and 30 mA, 0.02° step and 5 s counting time in the range 15–60°. The presence of a monochromator in the diffracted beam greatly enhanced the signal to noise ratio, giving an almost zero, flat background. In these conditions fine details of the pattern could be resolved, achieving an exhaustive interpretation and phase identification.

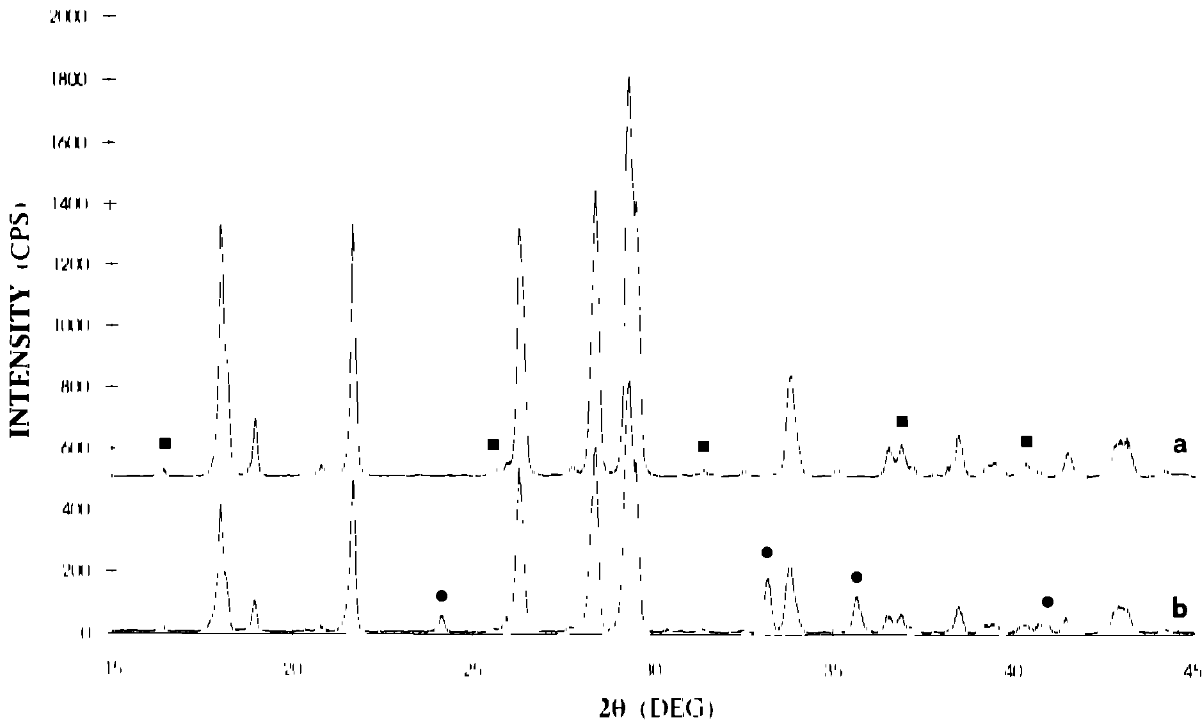


Fig. 1. XRD patterns of (a) original and (b) Fe_2O_3 contaminated supports, both treated for 3h at 1200°C. ■ $Al_6Si_2O_{13}$, ● Fe_2O_3; other peaks: $Mg_2Al_4Si_5O_{18}$.

A Cambridge Stereoscan 200 scanning electron microscope was used for SEM-EDS analysis.

3 Results

As shown by XRD phase identification (Fig. 1(a)), the original support was made of the synthetic cordierite or β-cordierite ($Mg_2Al_4Si_5O_{18}$, orthorhombic Powder Diffraction File (PDF) # 13-294[11]) with a small fraction of mullite ($Al_6Si_2O_{13}$, PDF # 15-776). $Mg_2Al_4Si_5O_{18}$ has also a hexagonal polymorph, indialite or α-cordierite (PDF # 13-293), whose peaks are superimposed to those of cordierite. For this reason, XRD is not able to exclude the presence of indialite.

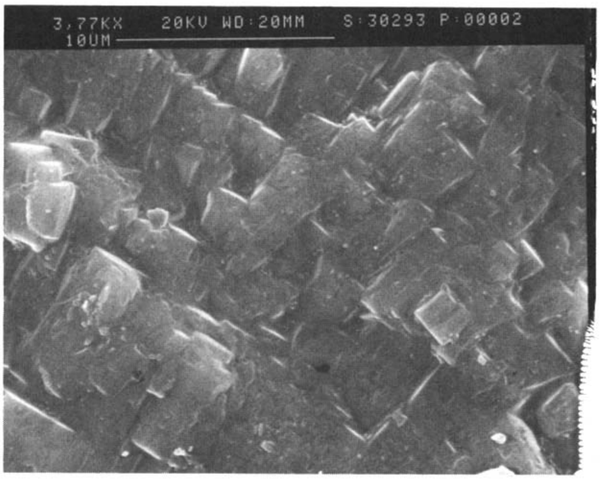
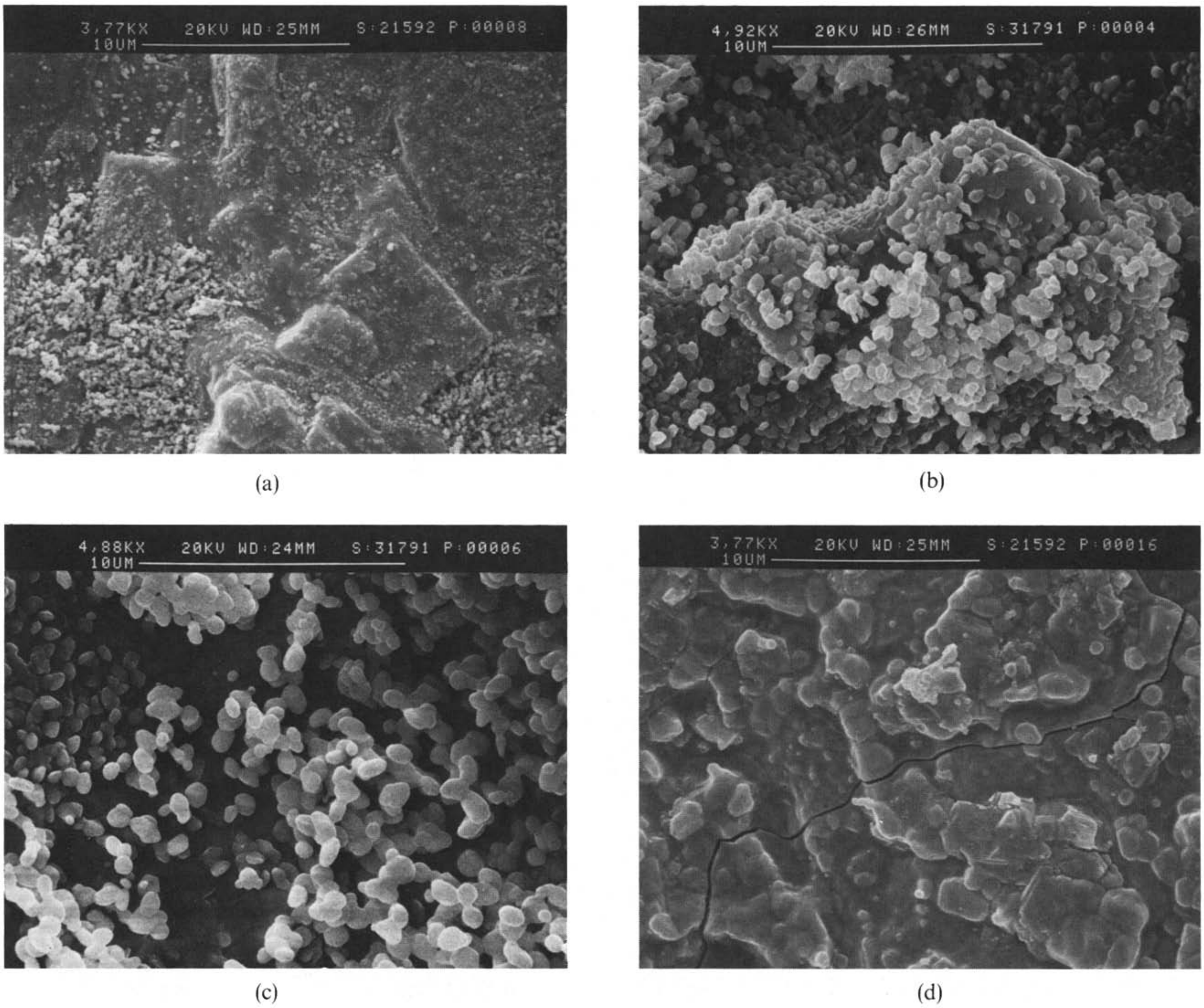


Fig. 2. SEM micrograph of the surface of original support treated for 3h at 1200°C.

The XRD patterns of the uncontaminated supports after 3h treatments at 800°C, 1000°C and 1200°C were unchanged. Also the surface morphology (Fig. 2) did not show visible differences. The only change occurred in the density: a porosimetric analysis showed a sintering effect, more evident after the 1200°C treatment.[10] In conclusion, the uncontaminated supports can be considered stable with respect to the studied thermal treatments.

Figure 1(b) shows the XRD pattern of a support contaminated by Fe_2O_3 after 3h at 1200°C. Besides cordierite and mullite, synthetic hematite (PDF # 33-664) was present. The same result was found for the same sample just after calcination (3h at 400°C). At higher temperatures the patterns were similar, with a progressive sharpening of hematite peaks due to coarsening. An intensity decrease of the cordierite signal was observed after the 1200°C treatment. SEM micrographs (Fig. 3) show the progressive growth of hematite crystals, which formed clusters dispersed on the surface of the samples. At 1200°C crystals appear to have partly reacted with the support, and a modified layer seems to be present.

After the thermal treatments, the presence of Fe-cordierite ($(Mg,Fe)_2Al_4Si_5O_{18}$, PDF # 9-472) could be expected. This phase, obtained by a partial substitution of Mg with Fe, is isomorphous to β-cordierite, with the same orthorhombic lattice and space group (*Cccm* (66)). Also in this case XRD cannot distinguish easily between the two phases, although the difference would be evident if a high percentage of Fe reacted with cordierite.[12]



(a) (b)

(c) (d)

Fig. 3. SEM micrographs of the surface of Fe_2O_3 contaminated supports calcined for (a) 3 h at 400°C and treated for a further 3 h at (b) 800°C, (c) 1000°C and (d) 1200°C

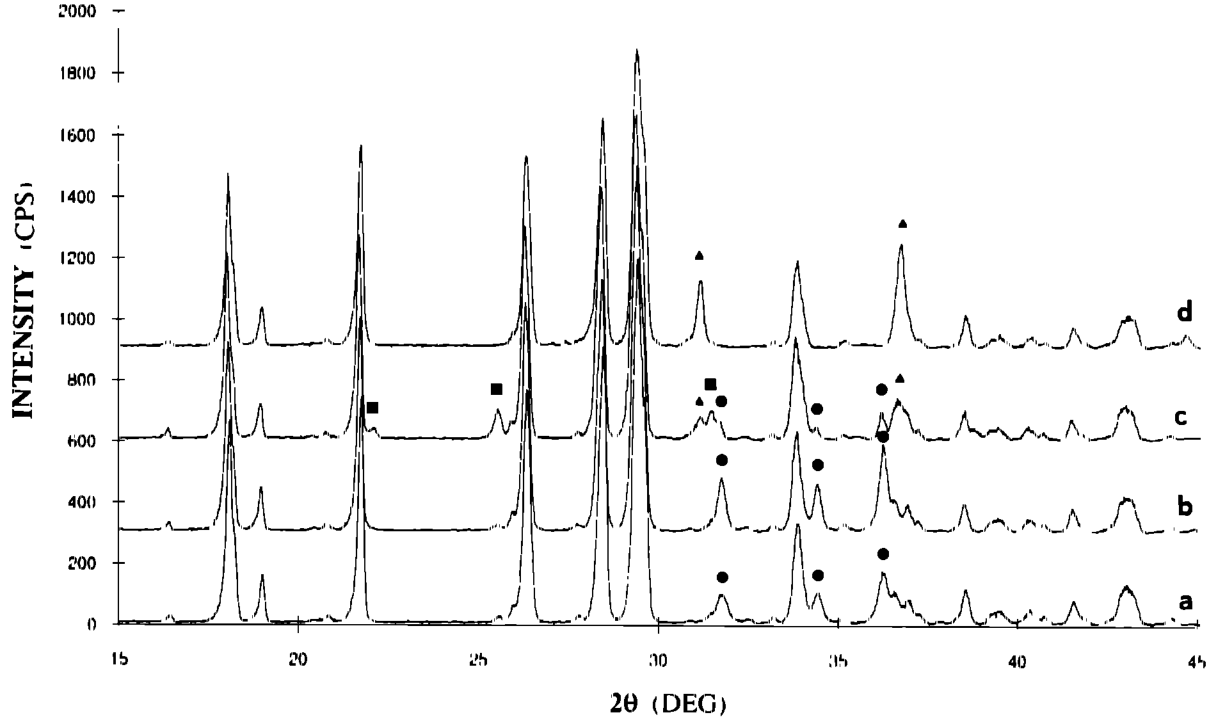
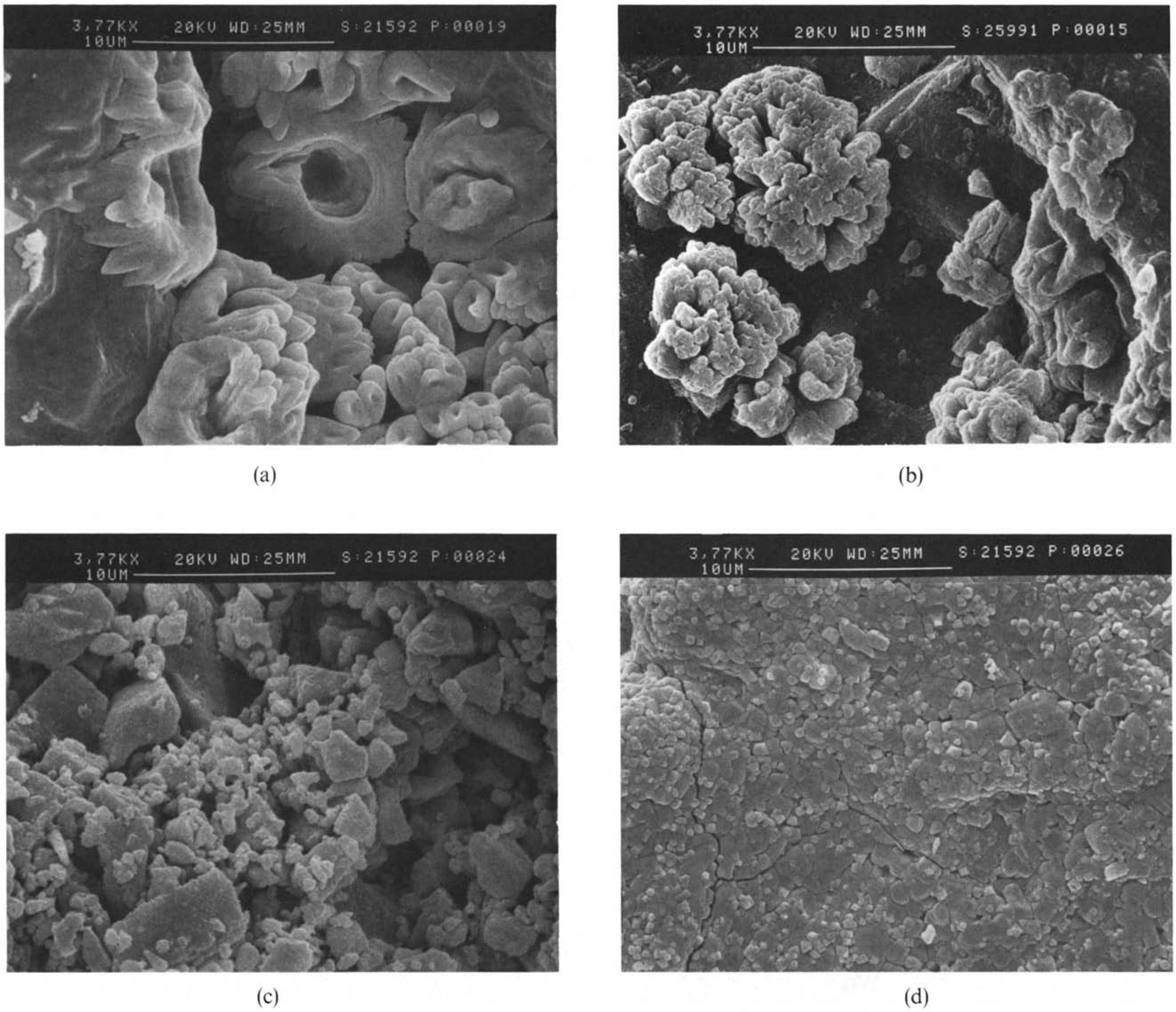


Fig. 4. XRD patterns of ZnO polluted supports after (a) calcination for 3 h at 450°C and further treatment for 3 h at (b) 800°C (c) 1000°C and (d) 1200°C ●, ZnO ▲, $ZnAl_2O_4$, ■ Zn_2SiO_4



(a) (b)

(c) (d)

Fig. 5. SEM micrographs of the surface of ZnO contaminated supports calcined for (a) 3 h at 450°C and treated for a further 3 h at (b) 800°C, (c) 1000°C and (d) 1200°C.

Moreover, as shown in Fig. 1, the pattern of Fe_2O_3 contaminated samples is the same, apart from hematite, as that of the original support.

The XRD spectra of ZnO polluted samples treated 3 h at 450°C, 800°C, 1000°C and 1200°C are reported in Fig. 4(a)–(d), respectively. The corresponding surface morphologies are shown by the SEM micrographs of Fig. 5. After calcination (Figs 4(a) and 5(a)) zincite (ZnO—PDF # 36-1451) formed. The 800°C treatment caused only a coarsening of zincite crystals, as suggested by the decrease of the broadening of ZnO profiles[10] (Fig. 4(b)).

At 1000°C ZnO reacted with the support producing two new phases (Fig. 4(c)): gahnite ($ZnAl_2O_4$—PDF # 50-669), with spinel-like structure, and willemite (Zn_2SiO_4—PDF # 37-1485). The peaks of the silicate showed remarkable differences of relative intensity respect to the PDF standard pattern. The micrograph, Fig. 5(c), shows that the surface of the support is homogeneously covered by several large crystals.

After the 1200°C treatment the only new crystalline phase was gahnite (Fig. 4(d)), in a larger amount. The presence of a very broad halo, centered at ~25° (not visible in Fig. 4), suggests the presence of a small fraction of glassy phase. As shown in Fig. 5(d), the surface was covered by a continuous layer incorporating crystals. Due to the presence of the reacted layer, the intensity of diffraction lines of the substrate components, that is cordierite and mullite, was progressively reduced after the thermal treatments. The effect was more evident at 1200°C, where mullite peaks were much reduced.

The XRD patterns of V_2O_5 contaminated samples thermally aged at 800°C, 1000°C and 1200°C were almost identical to each other. As shown in Fig. 6 for the sample treated 3 h at 1000°C, V_2O_5 reacted completely with the support, producing three new crystalline phases: MgV_2O_6 (PDF # 34-0013), AlV_2O_4 (PDF # 25-0028) and SiO_2 cristobalite (PDF # 39-1425). The surface of all samples (Fig. 7), was covered by several crystals with different shape, that were preferentially found within surface porosity.

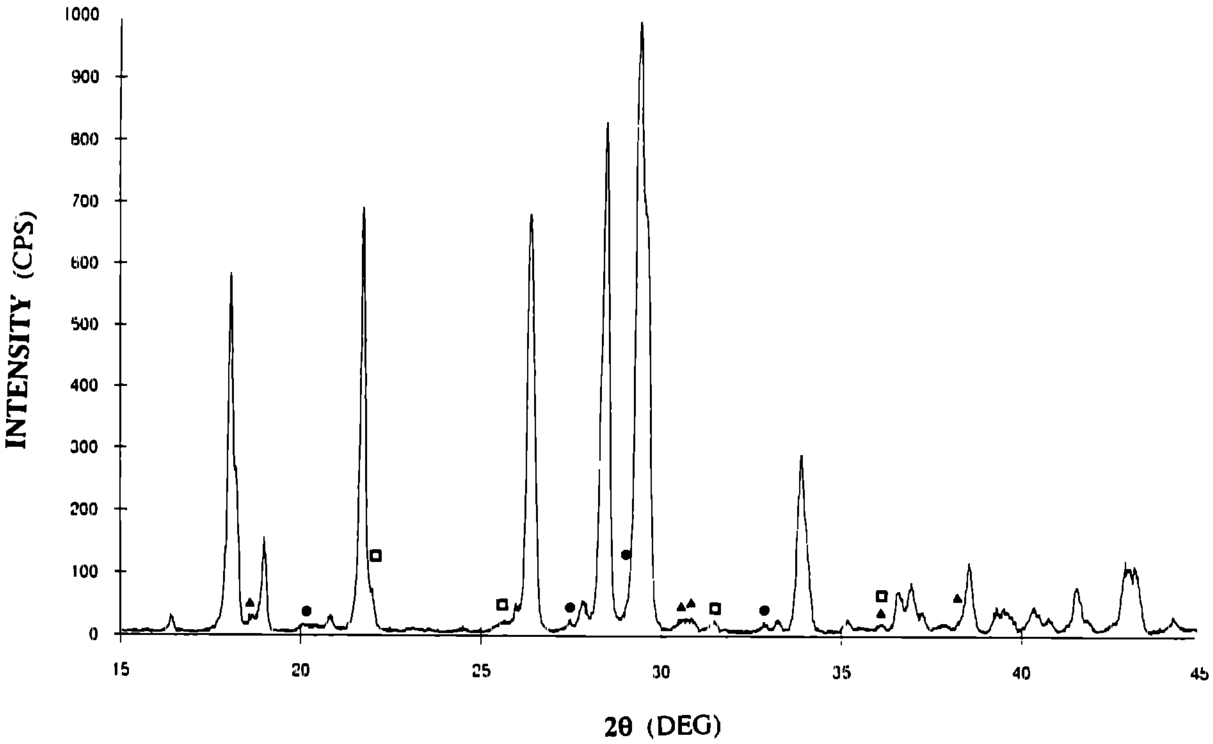


Fig. 6. XRD pattern of V_2O_5 contaminated support treated for 3 h at 1000 C ● MgV_2O_6 ▲ AlV_2O_4 □, SiO_2 cristobalite

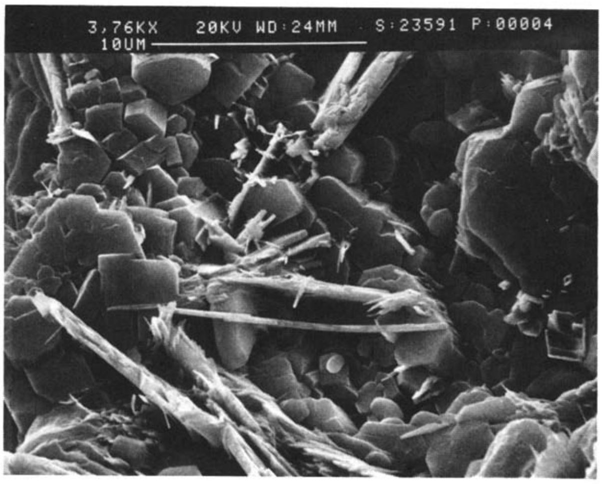


Fig. 7. SEM micrograph of the surface of V_2O_5 contaminated support treated for 3 h at 1000 C

4 Discussion

XRD analysis showed that iron oxide did not react with the substrate in the studied temperature range However, it is known that iron oxide tends to reduce the liquidus temperature of cordierite,[12] thus, the intensity decrease observed in the pattern of the sample treated at 1200 C and the relative surface morphology (Fig. 3) could indicate that a surface modification process started at this high temperature

No decomposition was observed in ZnO polluted samples treated at 800 C, the sharpening of zincite peaks suggests only coarsening of crystals At 1000 C, Zn spinel ($ZnAl_2O_4$) and Zn orthosilicate (Zn_2SiO_4) formed, while a zincite residual is still present While the Zn spinel pattern fits very well peak positions and relative intensities of the PDF # 50 699 standard, willemite shows remarkable differences in the intensities respect to the PDF # 37 1485 standard The reason is the partial substitution of Zn with Mg. In fact, even though Zn_2SiO_4 (phenacite group) is not isomorphous to Mg_2SiO_4 (forsterite, olivine group), it is known that willemite can accommodate up to 7% Mg in Zn sites.[13] As the Zn–Mg substitution changes the scattering factor, peak intensities change whereas the positions are less influenced

The phase evolution during the 1200 C treatment shows a close analogy with that observed for Na_2O contaminated supports.[5] In that case Mg spinel ($MgAl_2O_4$) and a glassy phase formed; similarly, the presence of ZnO led to the formation of Zn spinel plus glassy phase The analogy is due to the ease of Zn–Mg substitution and to the fact that both Na and Zn lower the liquidus temperature of SiO_2 based glasses. Therefore it can be supposed that a liquid phase formed at grain boundaries at 1200 C, which resulted in an amorphous phase after cooling The amorphous phase should be a SiO_2 based glass The lowering of the intensity of cordierite XRD reflections confirms this hypothesis. Mullite should take part to the reaction, by forming the observed Zn spinel.

The reaction of the cordierite support with V_2O_5 produced the same compounds at 800 C, 1000 C and 1200 C. This oxide, which has a low melting point (800 C), reacted completely in this temperature range, producing magnesium vanadate, alum-

Table 2. Modulus of rupture (MOR) from four point bending test: original and contaminated supports[10]

Treatment time and temperature	*Original support MOR (MPa)*	*ZnO contaminated MOR (MPa)*	*V_2O_5 contaminated MOR (MPa)*	*Fe_2O_3 contaminated MOR (MPa)*
	4.02 ± 0.24	3.55 ± 0.42[a]		2.91 ± 0.13[b]
3h 800°C	3.89 ± 0.18	3.50 ± 0.19	5.16 ± 0.77	2.89 ± 0.24
3h 1000°C	3.59 ± 0.09	3.91 ± 0.14	5.03 ± 0.42	2.70 ± 0.09
3h 1200°C	3.93 ± 0.21	3.94 ± 0.24	4.33 ± 0.36	3.28 ± 0.15

[a] Sample calcined 3h at 450°C.
[b] Sample calcined 3h at 400°C.

mium vanadate and crystalline silica. Contrary to what was found for ZnO, CaO and Na_2O contamination, no silicate crystals formed. V_2O_5 preferentially forms compounds with MgO and Al_2O_3, SiO_2 forms as the result of these reactions.

This result agrees with the Lux–Flood acid-base theory of molten salt oxide reactions reported in Ref. 14. The various oxides all have a certain acid–base character and the more acidic oxides can displace less acidic oxides from combination with basic oxides. For example, it is commonly seen in hot corrosion of superalloys containing Mo that MoO_3 formed by oxidation of Mo can displace SO_3 from sodium sulfate in the surface salt layer, producing sodium molybdate:

$$Na_2SO_4 + MoO_3 \rightarrow Na_2MoO_4 + SO_3$$

This theory has proved successful in explaining the differences in hot corrosion of scandia- and yttria-stabilized zirconia coatings by V_2O_5. In the present case the salt in question is cordierite. The differences in the nature of the crystalline products formed following V_2O_5 pollution can be explained taking into account that V_2O_5 is the most acidic oxide and therefore the most able to displace SiO_2 from combination with the basic MgO and the amphoteric Al_2O_3 oxides.

However, the presence among the reaction products of AlV_2O_4, in which vanadium is in an oxidation state lower than +5, indicates that the reaction is more complex, involving a disproportionation. The greater reactivity of the V_2O_5 pollutant can also be explained considering that its melting point is 690°C. Therefore, unlike Fe_2O_3 and ZnO, in the temperature range of heat treatment (800–1200°C) V_2O_5 is liquid.

Previous work showed that the pollution of cordierite supports can cause remarkable changes in their mechanical properties. The modulus of rupture (MOR) measured by four point bending test was strongly reduced in Na_2O contaminated samples, especially after the 1200°C treatment, whereas the presence of CaO resulted in an increase in strength. The lowering of MOR can be explained considering the thermal expansion mismatch between the modified surface layer and the bulk. Cordierite has a thermal expansion coefficient ($(0.7$–$1) \times 10^{-6}$ ($°C^{-1}$)) which is always lower than that of the products of the reaction with the examined pollutants; the formation of a continuous layer of modified material can lead to a crack initiation after thermal treatments and to embrittlement of the supports. In contrast, the formation of crystalline phases inside surface porosity, as observed in CaO contaminated samples, has a toughening effect that leads to increased strength.

This mechanism is also valid for the results of the present investigation. MOR values relative to V_2O_5, Fe_2O_3 and ZnO polluted supports, taken from Refs 6, 7 and 10, are reported in Table 2. V_2O_5 contaminated samples had MOR ~25% higher than original supports after each thermal treatment because of the preferential crystallization of new phases inside surface pores. In spite of the analogy with Na_2O polluted supports, the presence of ZnO did not influence MOR. This can be attributed to two main factors: firstly, there is much less glass at 1200°C with respect to Na_2O contaminated samples, and secondly, it is well known that the mechanical properties of SiO_2 glass are enhanced by the addition of ZnO. Fe_2O_3 contaminated samples treated at 800°C and 1000°C exhibited a MOR ~20% lower that the original supports. The reason is not clear, if it is considered that, as shown by XRD analysis, iron oxide did not react at all with cordierite. Taking into account that the reduction was recorded also for the sample only calcined, the MOR lowering could be linked to surface flaw modification due to the pollution process. The MOR of samples treated at 1200°C was slightly higher (~10% less than original supports). As shown by XRD and SEM, this is probably connected with the surface modifications of the substrate that started to react with iron oxide at this temperature.

5 Conclusion

The effect of Fe_2O_3, ZnO and V_2O_5 contamination on the stability and mechanical properties of cordierite catalysts supports, after thermal treatments in the operating temperature range of diesel particulate filters, was much different. Iron oxide did not react strongly with the supports, even if reaction products were not identified by XRD analysis, after 3 h at 1200°C the overall decrease of XRD signal and the surface morphology suggest that hematite started to interact with the cordieritic substrate. Zincite started to react at 1000°C, forming (Zn,Mg) orthosilicate and Zn spinel; at 1200°C the behaviour of the ZnO polluted samples was similar to that of the already studied Na_2O polluted ones, with the formation of spinel ($ZnAl_2O_4$ and $MgAl_2O_4$ for the two pollutants, respectively) and a small fraction of glassy phase. V_2O_5 reacted completely with the support forming, at all studied temperatures, magnesium vanadate, aluminium vanadate and cristobalite. The differences in reactivity and nature of the reaction products were explained considering the low melting point of V_2O_5 and its acidic character.

The mechanical properties of the contaminated supports after the various thermal treatments, were strongly influenced by the morphology of the modified layer and its thermal expansion coefficient. Due to the low thermal expansion coefficient of the cordierite substrate, the formation of a continuous layer of modified material always led to thermal expansion mismatch, that decreased the strength of the supports. On the other hand, the preferential crystallization of the decomposition products inside surface porosity, found for CaO and V_2O_5 contaminated samples, enhanced the mechanical properties of the cordierite catalyst supports.

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References

1. Owate, I. O. & Freer, R., The electrical properties of some cordierite glass ceramics in the system $MgO-Al_2O_3-SiO_2-TiO_2$. *J. Mat. Sci.*, **25** (1990) 5291-7.
2. Pilletteri, V. J., Case, E. D. & Negas, T., Laser surface melting and cutting of cordierite substrates. *J. Mat. Sci. Lett.*, **9** (1990) 133-6.
3. Lachman, I. M., Bagley, R. D. & Lewis, R. M., Thermal expansion of extruded cordierite ceramics. *Ceram. Bull.*, **60**(2) (1981) 202-5.
4. Centro Ricerche Fiat, Orbassano (To). Private communication.
5. Scardi, P., Sartori, N., Giachello, A., Demaestri, P. P. & Branda, F., *Ceram. Int.*, **19** (1993) 105-11.
6. Agostini, A., De Portu, G., Guicciardi, S., Borello, C., Demaestri, P. P. & Giachello, A., Characteristics of porous cordierite traps intentionally contaminated with calcium and zinc. In *Proceeding of the 4th International Symposium on Ceramic Materials and Components for Engines*, Goteborg, Sweden, 1991.
7. Agostini, A., De Portu, G., Guicciardi, S., Borello, C., Demaestri, P. P. & Giachello, A., Effects of sodium and iron on the thermo mechanical properties of porous cordierite traps for diesel engines. In *Proceeding of the European Ceramic Society, Second Conference (ECERC'2)*, Augsburg, Germany, 1991.
8. Cook, L. P., Bonnell, D. W. & Rathnam, D., Model for molten salt corrosion of ceramics. In *Ceramic Transactions, Corrosion & Corrosive Degradation of Ceramics*, Vol. 10, ed. R. E. Tressler & M. McNallan. The American Ceramic Society, Columbus, OH, 1990, pp. 251-78.
9. Jones, R. L., Hot corrosion resistance of scandia stabilized zirconia coatings. In *Ceramic Transactions, Corrosion & Corrosive Degradation of Ceramics*, Vol. 10, ed. R. E. Tressler & M. McNallan. The American Ceramic Society, Columbus, OH, 1990, pp. 291-308.
10. Sartori, N., Microstructural study of cordierite used in catalytic traps for the reduction of emission from diesel engines. Thesis, University of Trento, Italy, 16 July 1992.
11. Powder Diffraction File (1988), Swarthmore, PA. International Center for Diffraction Data.
12. Kim, Y. H., Mercurio, J. P. & Gault, C., Synthesis, formation mechanisms and polymorphism of iron and/or alkali substituted cordierites. *Ceram. Int.*, **1** (1985) 27-31.
13. Winchell, N. A. & Winchell, H., *Optical Properties of Artificial Minerals*. Academic Press Inc., NY, 1964, p. 300.
14. Jones, R. L., Williams, C. E. & Jones, S. R., Reaction of vanadium compounds with ceramics oxides. *J. Electrochem. Soc.*, **133** (1986) 227-30.