

## Microwave and catalysis as process integration for diesel soot abatement

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Microwaves heating and catalysis have been proposed as an integrated process to get fast diesel particulate filter regeneration without occurring in filter failure. The choice of the filter composition, catalytic active species and support material is a key parameter for optimal energy handling. In this work the effect of the catalyst support on the activity of Cu/V/K catalyst towards soot oxidation in the presence of microwaves was investigated. Results shown that in the presence of an active catalyst supported on a very good microwave absorbing oxide, the overall soot conversion is achieved in a very short time and with lower energy supply with respect to the uncatalytic case.

### 1. Introduction

Diesel particulate filters (DPF) are considered the most effective devices for the control of diesel particulate emissions. A requirement for the reliable operation of the DPF, however, is the periodic and/or continuous regeneration of the filters (Mayer, 2003). While microwave heating has been considered a potential active regeneration method for the DPF, past studies on the technology have identified several technical problems leading to filter failure. The problems are mainly associated with the use of inappropriate filter materials for the microwave system and the generation of local hotspots due to uneven microwave heating, resulting in the physical damage to the filters (Ning and Yongsheng, 1999). Indeed, high microwave power is usually required to achieve high filter regeneration efficiency, but we demonstrated (Palma *et al.*, 2002), that temperature controlled regeneration can avoid high thermal stresses inside the filter. Therefore, it is necessary to develop a technology employing a microwave-absorbing filter material coupled with an effective waveguide design for the reliable regeneration of DPF.

To this aim, few attempts combine microwave heating with catalysis in the DPF regeneration [Walton *et al.*, 1990; Ma *et al.*, 1997; Zhang-Steenwinkel *et al.*, 2004, 2005]. We also investigated (Ciambelli *et al.*, 2003; Palma *et al.*, 2004; Palma *et al.*, 2007) the possibility of combining catalytic and permittivity properties of the trap components (catalytic active species and ceramic foam) with the microwave absorbing properties of soot in order to enhance the performance of soot loaded filter regeneration, without occurring in filter failure. In this work, the effect of the catalyst support on the activity of Cu/V/K catalyst towards the oxidation of soot in the presence of microwaves was investigated. A MW apparatus was designed and optimized in order to perform a screening of catalysts for soot oxidation. Activity tests both at controlled heating rate and at fixed power supplied (900 W) were performed.

## 2. Experimental

### 2.1 Materials

Catalysts samples were prepared by supporting the active species of Cu/V/K catalyst on different ceramic materials: Al<sub>2</sub>O<sub>3</sub>: high purity alumina; Al<sub>2</sub>O<sub>3</sub> (92%): 92% Al<sub>2</sub>O<sub>3</sub> + 8% SiO<sub>2</sub>; SiC: high purity silicon carbide; SiC (50%): 50% SiC + 40.5% Al<sub>2</sub>O<sub>3</sub> + 9.5% SiO<sub>2</sub>; TiO<sub>2</sub>: 98% TiO<sub>2</sub> + 2% SiO<sub>2</sub>; Cordierite; PSZ(Mg): 97% ZrO<sub>2</sub> + 3% MgO. All catalysts were prepared by wet impregnation with aqueous solution of inorganic salts: NH<sub>4</sub>VO<sub>3</sub>, KCl and CuCl<sub>2</sub>·2H<sub>2</sub>O in the molar ratio Cu:K:V= 2:2:1. The suspension was stirred and heated at 573 K for 2 h and then dried at 393K for 2 h. The powder catalyst was calcined in static air at 973 K overnight. Soot was collected directly at the exhaust of a gas-oil burner (commercial gas-oil: H/C molar ratio = 1.75; S content = 0.05 wt%).

### 2.2 Apparatuses and procedures

In order to perform the catalyst screening in the presence of microwaves, a MW apparatus, reported in Figure 1, was specifically designed. The core of the apparatus is a MW system (Fricke und Mallah) including: i) a power supply that allows to smoothly and stepless adjust the magnetron output power up to 2000 W, driven by an external analog signal; ii) a 2.45 GHz water cooled 2 kW Magnetron head, fitted on a suitable launcher.

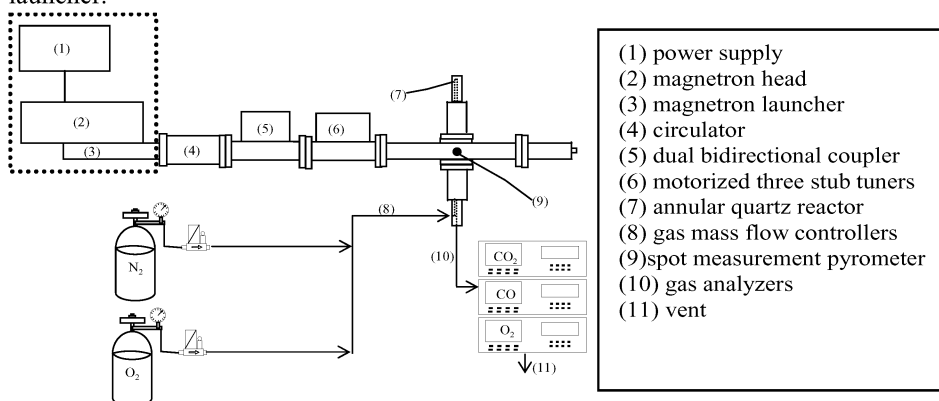


Figure 1. Scheme of the apparatus for catalyst screening in the presence of microwaves.

The latter is connected to a circulator with a water dummy load in order to protect the MW generator from the reflected power. The forward and the reflected power are measured by a dual bidirectional coupler fitted on a waveguide at the circulator output. The output signal from the coupler is linearised and amplified. Moreover, a motorized three stub tuner is fitted on the waveguide at the coupler output in order to match the load impedance and minimize the amount of reflected power. A quartz annular reactor (De=18 mm, Di=15 mm) is located in the centre of the waveguide, perpendicular to the direction of MW propagation, in the region of the maximum field. This particular geometry for the MW reactor was chosen in order to minimize the temperature radial gradient inside the catalytic bed. The sample temperature is measured by an optical pyrometer (Raytek), with a spot of about 4 mm, on the external reactor surface. The pyrometer is connected to a PID programmer to control the incident power. The inlet gas mixture was fed to the reactor by mass flow controllers (Brooks) and the reactor

outlet was sent to specific analysers (ABB, Uras 14 and Magnos 106) to continuously detect CO, CO<sub>2</sub> and O<sub>2</sub> concentrations.

The activity tests in the presence of microwaves were carried out on mixtures of soot and catalyst obtained by carefully grinding the two components in an agate mortar (tight contact). The initial amount of soot loaded was about 25 mg. The catalyst-soot mixture was diluted with quartz powder (180-355 μm) in a mass ratio of about 10. Typical condition test are the following: i) fixed power supplied (900 W) and initial catalyst-soot mass ratio of 30; ii) controlled heating rate (20 K/min) with a continuously variable power supplied and initial catalyst-soot mass ratio of 10; inlet gas flow rate (10.5%vol O<sub>2</sub> in N<sub>2</sub>) 1000 (STP)cm<sup>3</sup>/min.

### 3. Results and discussion

Results of uncatalytic and catalytic (Cu/V/K-TiO<sub>2</sub>) soot oxidation tests in the presence of MW performed supplying constant power (900 W) are shown in Figure 2, in terms of CO+CO<sub>2</sub> concentration, temperature and incident (Pi), reflected (Pr) and absorbed (Pa) microwave power.

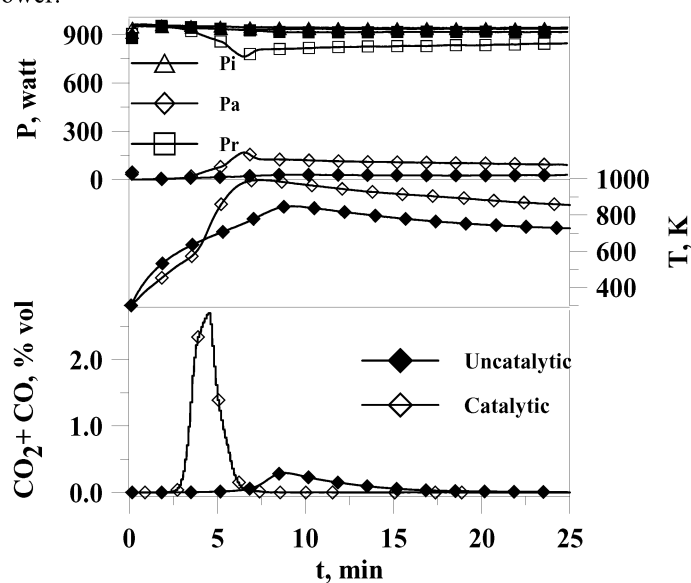


Figure 2 Uncatalytic and catalytic (Cu/V/K-TiO<sub>2</sub>) soot oxidation tests in the presence of microwaves supplying a 900 W constant power.

Initially, up to a temperature of about 450 K, the uncatalytic system shows a higher heating rate (160 K/min) compared to the catalytic one (80 K/min), even if the soot oxidation reaction has not yet started. This is probably due to the lower absorbing properties of catalyst with respect to soot. After 2 min, the heating rate of the uncatalytic system decreases to about 40 K/min. The uncatalytic soot oxidation starts at a temperature of 770 K (after 6.5 min), but at 20% carbon conversion (850 K), the absorbed microwave power is no longer sufficient to heat the system and the soot oxidation rate decreases with the temperature. Therefore, the overall carbon conversion (after 16 min) is about 38%. In the case of the catalytic system, soot oxidation starts at a

temperature of 520 K (2.5 min). At 660 K, where CO+CO<sub>2</sub> concentration reaches a maximum value, the heating rate quickly increases to 170 K/min because of the exothermic heat generated by the catalytic soot oxidation reaction. The rapid temperature increase entails an increase of absorbed microwave power, as will be shown in the following (Figure 6). In this case after only 6.5 min the soot oxidation is completed.

The profiles of microwave soot oxidation at controlled heating rate for Cu/V/K catalysts supported on different ceramic materials are reported in Figure 3 in terms of CO+CO<sub>2</sub> concentration as function of temperature. It is shown that the soot ignition temperature for all the catalysts is in the range of 540-580 K and the maximum oxidation rate in the range of 655-705 K, except for Cu/V/K-SiC which is less active with a maximum oxidation rate occurring at 780 K. All the catalysts give total soot conversion and a CO<sub>2</sub>/CO ratio in the range of 15-20. In the absence of catalyst the soot ignition temperature is about 750 K and the CO<sub>2</sub>/CO is equal to 1.8.

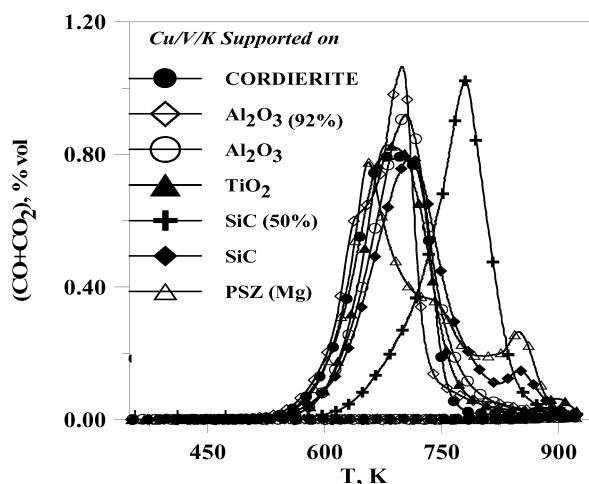


Figure 3 Catalytic soot oxidation by microwaves on Cu/V/K supported on different ceramic materials (20K/min controlled heating rate tests).

The energy required to reach a given conversion for the uncatalytic and catalytic soot oxidation was evaluated and reported in Figure 4. It increases with soot conversion, being the soot the main microwave absorber. However, the presence of the catalyst allows the energy requirement be reduced with respect to the uncatalytic oxidation. In particular, the Cu/V/K-TiO<sub>2</sub> sample results the most efficient catalyst.

In the absence of microwaves the energy saving obtained in the presence of the catalyst is due to the specific activity towards soot oxidation which allows to reach the same conversion at lower temperature and hence in a shorter time with respect to the uncatalytic oxidation. In this particular case, in order to evaluate the contribute in terms of specific microwave absorbing properties of each catalyst, the energy required to reach 30, 50, 70 and 90% carbon conversion was related to the temperature at which this conversion is reached during thermogravimetric (TGA) oxidation tests (Figure 5).

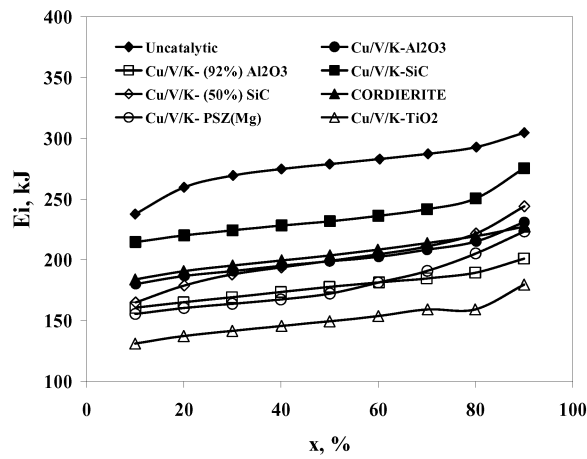


Figure 4. Microwave energy required to reach different soot conversion during catalytic and uncatalytic soot oxidation at controlled heating rate.

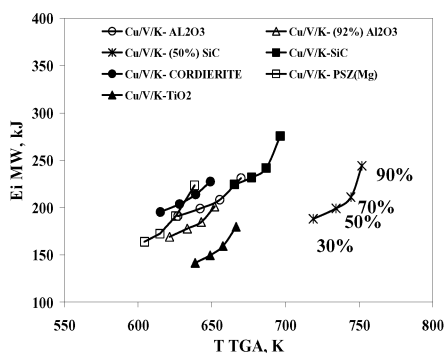


Figure 5. Microwave energy required to reach different soot conversion as function of temperature evaluated by TGA tests.

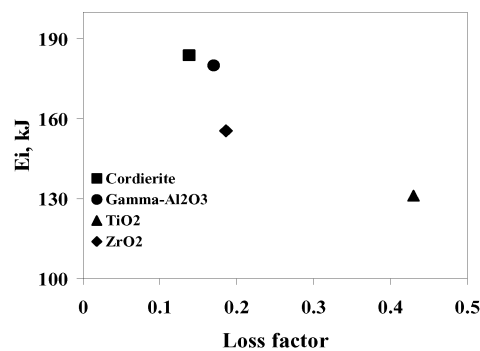


Figure 6. Microwave energy required to reach 10% soot conversion as function of loss factor for different materials.

In particular, experimental results do not correlate with the specific catalytic activity obtained by TGA tests, but a different scale of energy requirement for a given soot conversion is obtained. Indeed, catalysts supported on PSZ(Mg),  $\text{Al}_2\text{O}_3$ , and cordierite allow to reach 30% carbon conversion at temperatures lower than Cu/V/K-SiC and CuVK-TiO<sub>2</sub>, while CuVK-TiO<sub>2</sub> is the most efficient in terms of energy required to reach this conversion. These results are in agreement with the literature (Ma *et al.*, 1997), where TiO<sub>2</sub> appears the most suitable catalyst support in comparison with different ceramic materials, promoting soot oxidation at low levels of microwave input power. Moreover, they suggest that the microwave absorbing properties of the ceramic support have a primary role together with the specific catalyst activity in the oxidation of soot.

In Figure 6 the energy required to reach 10% of soot conversion was related to the dielectric properties of the ceramic powder support in terms of loss factor (Ma *et al.*, 1997). It is observed that cordierite, having the lowest loss factor (0.138), requires the highest energy supply (184 kJ), while TiO<sub>2</sub> powder requires the lowest supply (130 kJ), having the highest loss factor (0.430).

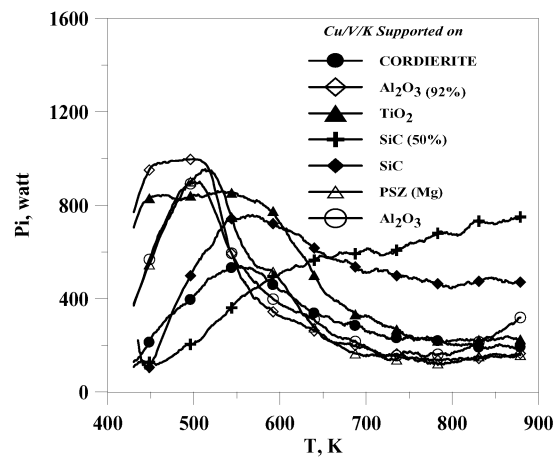


Figure 7. Incident microwave power as a function of the catalyst temperature.

Furthermore, the  $P_i$  required after soot conversion to maintain the set temperature of the catalyst alone was evaluated for all the Cu/V/K supports through experiments at controlled cooling (Figure 7). Results show that for all samples, except for SiC, at lower temperatures (400-600 K) it is necessary an high  $P_i$  to maintain the requested temperature. However these high values do not affect the energy evaluation for soot conversion, because in this temperature range the soot conversion is very low and the very good soot microwave absorption properties are predominant. Beyond 700 K, the  $P_i$  values decrease for all samples, except for SiC again. This behaviour is very significative in the computation of the energy required for soot conversion, because in this temperature range, the soot is almost completely burned and the catalyst microwave absorbing properties become predominant. Hence, the high power requested at high temperatures of SiC supported catalyst is responsible for the lower energy efficiency of these catalysts as well as for their lower activity.

#### 4. Conclusions

Reliable operation of a DPF can be assured when regeneration by microwaves are combined with a catalyst having either specific activity for soot oxidation and good MW absorption properties. Experimental results indicate that the microwave absorbing properties of ceramic supports have a primary role like the specific catalyst activity. In particular, with respect to the uncatalytic case the energy saving obtained in the presence of the catalyst is due to the specific activity towards soot oxidation which allows to reach the same conversion at lower temperatures and hence in a shorter time. In addition, tests performed with different ceramic powder supports confirm that the material with the highest value of the loss factor (TiO<sub>2</sub> powder) requires the lowest energy supply to reach a given soot conversion.

#### 5. References

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