

# A DRIFT SPECTROSCOPIC STUDY OF THE ALKALI CATALYZED SOOT AND FULLERENE C60 OXIDATION

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## Introduction

FT-IR and in particular Diffuse Reflectance Infrared Fourier Trans-formed (DRIFT) spectroscopy is a powerful tool for the analysis of oxidic functionalities on carbonaceous materials. The observed surface oxygen complexes (SOCs) are generally accepted to play an essential role in the oxidation mechanism. Interactions between alkali metal oxides and SOCs have been described by *e.g.* [1-3]. Mims and Rose [1] have proposed a catalytically active potassium complex, based on potassium phenoxide. A similar proposition for the active species has been postulated by Cerfontain and Moulijn [2], based on a spectroscopic study. However the observed absorption frequencies are not quite consistent with reference compounds: potassium phenoxide functionalities were assigned to absorption frequencies located around  $1100\text{ cm}^{-1}$ , whereas important frequencies of  $\text{KOC}_6\text{H}_5$  occur at higher wavenumbers. An exotic compound  $(\text{C}_6(\text{OK})_6)$  has been proposed by Freriks *et al.* to explain spectroscopic observations [3], but an unambiguous interpretation of the bands in the  $1100\text{-}1200\text{ cm}^{-1}$  region has not been presented. In this abstract, various spectra of the alkali metal catalyzed soot and fullerene C60 oxidation are presented, including an extended interpretation of the spectra.

## Experimental

Printex-U (a model soot, provided by Degussa) was used to perform the oxidation studies [4]. Sublimed fullerene C60 was purchased from Bucky USA. Potassium benzoate was used as received from Aldrich. Analytical grades of the alkali metal nitrates were used to impregnate the soot, corresponding to 10 wt% of the most stable oxide ( $\text{Me}_2\text{O}$ , in which Me is K, Na, Rb, and Cs) [4]. Physical mixtures were prepared by ball milling various potassium salts with soot or Fullerene C60 in a mass ratio of 2:1 for one hour in an agate ball mill to establish 'tight contact' conditions. Partial conversion of the impregnated samples was accomplished isothermally at 575 K in

the so-called six-flow reactor setup [4].

DRIFT spectra were recorded on a Nicolet Magna 550 spectrometer equipped with a DTGS detector and a Spectratech DRIFT 'Collector' accessory and recorded as described elsewhere [5].

## Results and Discussion

DRIFT spectra of partially converted alkali metal impregnated soot samples are shown in figure 1.

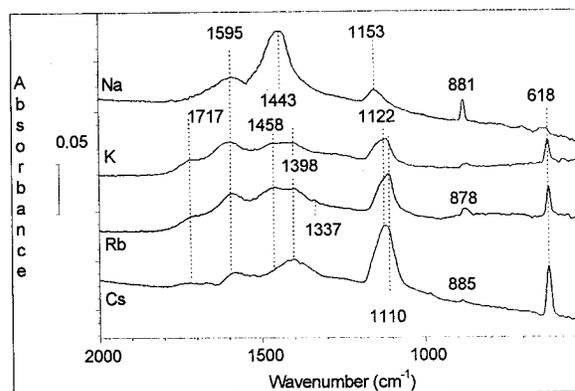
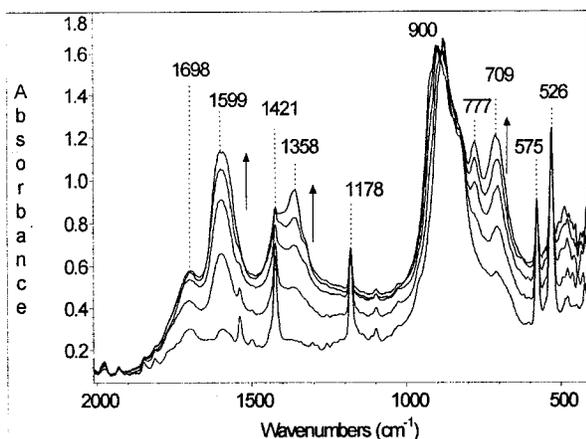


Figure 1. DRIFT spectra of partially converted Na-, K-, Rb- and Cs-impregnated Printex-U samples, converted to approximately 90%.

Several absorption frequencies, different from those observed in spectra of non-catalytically oxidized soot ( $1250$ ,  $1605$  and  $1735\text{ cm}^{-1}$ ) [4, 5], can be observed. The relative intensity of the absorption bands in the  $1100\text{-}1150\text{ cm}^{-1}$  region, located at approximately  $1398\text{ cm}^{-1}$ , and located at  $620\text{ cm}^{-1}$  seems to increase in the series  $\text{Na} < \text{K} < \text{Rb} < \text{Cs}$ , whereas the contribution of the  $1450\text{ cm}^{-1}$  and  $881\text{ cm}^{-1}$  bands seems to decrease in this series. The  $1398\text{ cm}^{-1}$  and  $1100\text{-}1150\text{ cm}^{-1}$  bands are composed of more than one single frequency. The  $1400\text{-}1480\text{ cm}^{-1}$  absorptions are assigned to bulk carbonate, which is confirmed by the bending vibrations of the free carbonate ion around  $880\text{ cm}^{-1}$ . Apparently, the amount of carbonate formed decreases in the series  $\text{Na} > \text{K} > \text{Rb} > \text{Cs}$ .

To prevent the possible interference of carbonate or nitrate vibrations of either  $\text{K}_2\text{CO}_3$  or  $\text{KNO}_3$ , with

spectral details of oxidized C60,  $K_2MoO_4$  was used to perform an *in-situ* DRIFT analysis of the catalytic C60 oxidation. The spectrum is shown in figure 2.



**Figure 2.** Development of the spectral features of fullerene C60 upon oxidation in air, catalyzed by  $K_2MoO_4$  at 625 K. Spectra were recorded (bottom to top) after 0, 5, 10, 15 and 45 minutes respectively.

Absorption frequencies at  $1698\text{ cm}^{-1}$ ,  $1599\text{ cm}^{-1}$ ,  $1358\text{ cm}^{-1}$ ,  $777\text{ cm}^{-1}$  and  $709\text{ cm}^{-1}$  are shown increase with time, which are significantly different from the absorptions observed in non catalytic C60 oxidation [5]: especially the  $1599\text{ cm}^{-1}$  band has a relatively higher intensity in the  $K_2MoO_4$  catalyzed C60 oxidation than in the uncatalyzed reaction. Major absorptions in the spectrum of potassium benzoate are located at  $1591\text{ cm}^{-1}$  (C=C stretch),  $1549\text{ cm}^{-1}$  (antisymmetric C=O stretch),  $1394\text{ cm}^{-1}$  (symmetric C=O stretch),  $837\text{ cm}^{-1}$  (C-O stretch) and  $708\text{ cm}^{-1}$  (-C=C- ring deformation). Hence, various spectral changes in figure 2 can be ascribed to the formation of potassium benzoate species.

The  $K_2MoO_4$  catalyzed oxidation of fullerene C60 was also followed by *in-situ* XRD using temperature intervals of 50 K in the range of 507-657 K. Major differences can be observed in the diffractogram recorded at 557 K. Several new lines can be assigned to  $K_2Mo_2O_7$  ([5] JCPDF [36-0347]). The absorption band at  $777\text{ cm}^{-1}$  in figure 2 can be assigned to this oxide.

The bands at  $1110\text{--}1153\text{ cm}^{-1}$  and  $618\text{ cm}^{-1}$  observed in figure 1, cannot be assigned to benzoate, nor to phenoxide species: major bands in the potassium phenoxide spectrum are located at 1467, at 1320, around 980, 780 and  $550\text{ cm}^{-1}$  [5]. Although a detailed discussion cannot be given here, various literature data describe the formation of potassium oxides upon catalytic carbon oxidation and a strong interaction of these clusters with  $CO_2$ . Absorption

bands at  $1010\text{--}1090$  and  $660\text{--}680\text{ cm}^{-1}$  (symmetric stretch and C-O bending modes) are IR forbidden in anhydrous  $K_2CO_3$  (free carbonate), but are IR active in monodentate or bidentate configurations of chemisorbed  $CO_2$  on transition metal oxide surfaces. Based on the location of the bands in figure 1, an assignment to monodentate  $CO_2$  might be given ( $\nu_4 = 1595\text{ cm}^{-1}$ ,  $\nu_1 = 1398\text{ cm}^{-1}$ ,  $\nu_2 = 1120\text{ cm}^{-1}$ , and  $\nu_3$  or  $\nu_5 = 620\text{ cm}^{-1}$ ). A multiple character of the  $\nu_2$  vibration has been observed in the spectra of cobalt-carbonato complexes, in agreement with the spectra in figure 1 [5]. Although the relative intensity of the bands in our spectra is not in agreement with literature data (the  $\nu_2$  vibration is usually small compared to the  $\nu_4$  and  $\nu_1$  vibrations), this might be related to the strong interaction of the alkali metal oxides with  $CO_2$ , which also explains the extremely low absorption frequency of the bending mode ( $618\text{ cm}^{-1}$ ), relative to  $CO_2$  adsorbed on the surface of transition metals.

## Conclusions

- Various absorption bands similar to those observed in the spectra of potassium benzoate have been identified in the DRIFT spectra of partially converted, alkali metal impregnated soot.
- $CO_2$ , chemisorbed on alkali metal oxide species, is suggested to cause the absorptions around  $1100\text{--}1150\text{ cm}^{-1}$  and  $620\text{ cm}^{-1}$ . Spectroscopic evidence for the formation of phenoxides was not found.
- $K_2Mo_2O_7$  has been identified in *in-situ* XRD experiments of  $K_2MoO_4$  catalyzed C60 oxidation, corroborating the possible formation of (non-crystalline) oxidic clusters and potassium benzoate species.

## References

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