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## **The role of lattice defects in the partial oxidation of methanol to formaldehyde over carbonaceous catalysts**

E. Sanchez-Cortezon, M. Dieterle, Y. Uchida, G. Weinberg, G. Mestl, M. Schur, R. Schlögl

Fritz-Haber-Institut der MPG, Abteilung Anorganische Chemie, Berlin

E-mail: [emilio@fritz-haber-institut.mpg.de](mailto:emilio@fritz-haber-institut.mpg.de)

### ***Introduction***

It has been demonstrated<sup>1</sup> that graphite catalyses the partial oxidation of methanol to formaldehyde while amorphous carbon samples such as carbon blacks and fullerene blacks do not catalyse this reaction. The proposed model is based on the presence of well crystalline basal planes which are correlated with the observed activity. It is believed that ionic oxygen species are present on these basal planes. These special O-species are suggested to be responsible for the methanol oxidation. Nevertheless, the different origins, surface areas and morphologies of the carbonaceous samples made it difficult to completely confirm this model, and to derive a structure-activity relationship. To determine the validity of this model, the starting material, graphite was submitted to mechanical activation. It is known in the literature<sup>2,3</sup> that mechanical milling introduces defects in a solid and results in an amorphisation. An increasing amorphisation of graphite should lead to a decrease of the catalytic activity. The combustion of the samples milled under various conditions was also conducted as a test reaction to study the mechanically induced increase in reactivity.

### ***Experimental and Results***

The samples in this study were prepared from graphite AF-spezial (99.5 C % purity, Kropfmühl). The mechanical activation was conducted in an agate centrifugal ball mill. The milling variables under study were: presence or absence of a non polar solvent, hexane, and the milling duration. The evolution of the structure was determined by X-ray diffraction in Debye-Scherrer geometry and by Raman spectroscopy with He-Ne-laser (632.8 nm) excitation. The specific surface area measurements were done with the three points BET method. The morphology was studied using scanning-electron-microscopy and high-resolution-transmission-electron-microscopy. The combustion measurements were conducted in a thermogravimetric analysis system. A tubular flow reactor (duran glass) with an inner diameter of 7.5 mm was used in the catalytic runs. A heating rate of 5K/min and an hourly-

space-velocity of  $4.6 \times 10^4 \text{ h}^{-1}$  were used. The products were monitored using an Ion-Molecule-Reaction-MS apparatus (IMR-MS 1100, ATOMIKA). The total flow in the experiments was set at 186 ml/min and the  $\text{N}_2:\text{MeOH}:\text{O}_2$  ratio varied from 85:16:1 to 20.25:2:1.

The characterisation of the samples indicated that the mechanical activation in absence of hexane considerably lowered the crystallinity of the carbon material, as indicated by the decrease of the crystallite size in the crystallographic [002] and [110] directions. On the other hand, milling in presence of hexane resulted in a material with a high surface area which still retained high crystallinity of the basal planes.

The combustion measurements for the samples milled in absence of hexane showed two main combustion peaks with activation energies of 156 and 190 kJ/mol, which could be assigned to combustion processes of defects and basal planes, respectively. In addition, milling in absence of hexane decreased the onset temperature of the combustion and increased the intensity of the defect induced peak. In contrast, only one combustion peak was observed after milling in presence of hexane with an activation energy of 190 kJ/mol.

The catalytic runs indicated that the progressive milling in absence of hexane decreased the activity to formaldehyde as compared to the „as is“ material. The yield to formaldehyde at 748K decreased from 12% to 5% after seven days of dry milling. On the other hand, milling in presence of hexane increased the yield to formaldehyde to 15%. Furthermore, the last mentioned and the „as is“ material did not show any significant changes in their structure after the catalytic runs. On the other hand, the samples milled in absence of hexane showed structural changes after catalytic runs. These samples showed after reaction a weight loss which was attributed to a decrease of the number of structural defects determined by X-ray diffraction.

### *Conclusions*

It could be demonstrated that carbon defects play a role in the partial oxidation of methanol. The gradual loss of long-range order in the graphite structure generated under dry milling conditions could be correlated with an increase in the defect combustion peak of 156 kJ/mol, and with a decrease in the overall activity to formaldehyde. Hence, the presence of defects are negative for this reaction. Milling under hexane conditions gave a high surface area crystalline material with a predominant combustion peak of 190 kJ/mol corresponding to



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the combustion of graphite. This material showed a high activity to formaldehyde due to its increased surface area and the preservation of intact basal planes.

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<sup>1</sup> E. Sanchez-Cortezon, R. Schoonmaker, U. Wild, D. Herein, R. Schlögl, Deutsche Kat. Tagung Leipzig, 1998 in press.

<sup>2</sup> U. Steinike, H-P. Hennig, KONA, 10, 15, 1992.

<sup>3</sup> T. Rühle, D. Herein, G. Weinberg, N. Pfänder, R. Schlögl. submitted to Ber. Bunsen Gesellschaft.