

# PREPARATION AND CHARACTERIZATION OF SYNTHETIC CARBON COATED MONOLITHIC CATALYSTS

*E. Crezee, C.S. Tjon Joen Sjong, F. Kapteijn, and J.A. Moulijn  
Industrial Catalysis, DelftChemtech, Faculty of Applied Sciences,  
Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands*

## Abstract

Carbon coated ceramic monoliths based on polyfurfuryl alcohol are described. A single dipcoating step resulted in a carbon load, after carbonization, of ca. 13 wt%. The obtained carbon is essentially microporous. Mesoporosity can be introduced by adding a pore-forming agent (PEG-5000) to the starting material, the carbon yielding precursors. Emphasis was laid on creating the right surface chemistry, since the oxygen surface complexes act as anchoring sites for the metal precursor  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  during catalyst preparation and as active centers in the selective oxidation of cyclohexanone. The supports have therefore been subjected to different oxidation treatments, like physical activation (air) and functionalization ( $\text{NaOCl}/\text{HNO}_3$ ) treatments. The surface chemistry of the obtained supports was studied by TPD-MS and DRIFT. A high metal loading (5.2 wt% Pt/C) and dispersion (43%) could be achieved for the Pt/C catalysts.

## 1. Introduction

Carbon has some characteristics that are very valuable and not attainable with any other support. These are the possibilities to tailor the physical/chemical surface properties of the support and to modify the nature of the metal/support interaction. Nevertheless, only a few large-volume catalytic processes currently use carbon-supported catalysts [1,2]. The major constraint on the use of carbon supports in advanced liquid-phase applications arises from the nature of the production process. The vast majority of carbons used as catalyst support are derived from naturally occurring precursors (e.g. coal, wood, etc.), which are converted to activated carbons by carbonization, to produce a char, and activation. The resulting materials have pore structures reflecting both the structure of the precursor and the activation process. Several problems arise in the use of these materials as catalyst supports. One of these problems is their large ash content, which after activation is concentrated on the carbon surface. These inorganic constituents may interact with the metal, affecting its catalytic activity and sintering resistance and even catalyze secondary reactions [3]. A further problem of these materials in catalyst production arises from the scale of the production process [4]. Activated carbons are generally produced on 1000's tonne

scale whereas the catalyst supports are used in small-scale processes requiring at most a few tonnes. The nature of the quality control required at these scales for the different applications tend to be very different and achieving reliable and reproducible properties in commercial activated carbons can be difficult. The ability to generate structured carbon particles is also limited by the process which normally uses high levels of pitch binders (up to 50 wt%) to achieve reasonable mechanical properties. This effectively limits the physical forms to simple granules or extrudates with only limited control over the macropore structure. The use of these structures in trickle-bed reactors is associated with high-pressure drops, potential channeling and other disadvantages.

The problems encountered above can be overcome by the use of carbon monoliths based on synthetic precursors. Compared to the conventional trickle-bed reactors, monolithic reactors provide the advantages of low-pressure drops, large external surface areas and short diffusion lengths [5]. From literature two types of synthetic carbon based monolithic structures are known, the integral type and the coated type. The integral monoliths are prepared by extrusion of the carbon precursor, i.e. phenolic resin, mixed with various additives. These additives, which include organic and inorganic powdered materials such as cordierite powder, cellulose fiber, polyester fiber, etc., make the resin extrudable. By varying the extrusion composition, monoliths with an activated carbon content ranging from 5 to 100 wt% can be fabricated [6]. Tennison [4] described a method to produce pure carbon monoliths using the Novolak (phenol-formaldehyde resin) resin-sintering route. The absence of ceramic materials results in a prominent shrinkage upon carbonization and difficult control of the 3D structure.

Different methods have been described in literature to prepare carbon coated monoliths [7]. The most frequently applied method is the dipcoating method. In principal the method is as follows [8]: the ceramic honeycombs are dipped in a high carbon yield polymeric solution of low viscosity, allowed to soak for a few minutes and then drained off the excess polymer, before being subjected to a drying and/or curing process. The coated honeycombs are then subjected to a carbonization and activation process. Different carbon precursors have been used, like phenolic [9] and furanic resins [10], polysaccharides

(sucrose and dextrose) [11] and polyfurfuryl alcohol [12]. Although the dipcoating method produces strong, durable honeycomb structures, it has the drawback that the carbon loading is relatively small even when highly porous honeycombs are being used. After carbonization and activation, maximum values for the carbon loading are being reported of ca. 20 wt% [6].

In this study carbon coated ceramic monoliths have been prepared based on polyfurfuryl alcohol. These supports have been applied to the three-phase hydrogenation of cinnamaldehyde [13] and the selective oxidation of cyclohexanone by air to dicarboxylic acids [14]. Since the activity and selectivity of latter process shows a significant dependence on the support characteristics [15], the surface chemistry of the carbon coated monoliths was optimized by applying different oxidation treatments. The porosity of the carbon supports was enhanced by the addition of a pore-forming agent (PEG-5000) to the polymerization mixture.

## 2. Experimental

### 2.1 Catalyst preparation

Carbon coated monolithic supports have been prepared according to a method developed by Vergunst et al. [12].

As a substrate cordierite monolithic supports are used. Cordierite, a magnesium alumino-silicate with a melting point of about 1738 K, has a thermal expansion coefficient comparable to that of carbon thereby increasing the stability of the formed composite [9]. The monoliths used in this study have square cells and a cell density of 62 cells/cm<sup>2</sup> and a wall thickness of 0.18 mm. The samples had a length of 5 cm and a diameter of 1 cm. Prior to coating the cordierite monoliths were heat treated for 3 hr in a static air oven at 1273 K to remove possible contaminants from the surface.

Furfuryl alcohol and pyrrole were used as carbon yielding precursors. The advantage of using these monomers over more complete polymerized resin as starting material, is that they are less viscous and as a consequence can be more easily blended [16]. Poly (ethylene glycol) methyl ether  $M_n=5000$ , abbreviated to PEG-5000, was used as a pore-former. In the initial step of the coating process the binders (90 ml furfuryl alcohol and 27 ml pyrrole) and the pore-former (0-90 ml PEG-5000) were blended to form a homogeneous fluid. The polymerization catalyst was concentrated nitric acid, which was carefully added stepwise to the mixture for 45 min. After catalyst addition, polymerization was continued for an hour. Since the mixture readily polymerized exothermally at ambient conditions, continuous stirring and cooling were necessary to avoid a thermal runaway reaction. The polymerization

temperature had to be maintained at 294 K. Intake of gas bubbles during mixing had to be avoided to ensure that the pores in the carbonaceous body would be formed only by liquid. Bubbles produce pores that are generally large with respect to the liquid formed pores. Furthermore, even very small bubbles in the blended mix tend to grow during subsequent steps involving heating; these bubbles may particularly cause cracking during carbonization.

The cordierite monoliths were dipcoated in the partially polymerized mixture and allowed to soak for 5 min. During this process, the fluid mixture was conditioned by cooling in ice to slow down the speed of the polymerization reaction and thereby maintaining a constant viscosity. After dipcoating, the excess solution was drained by nitrogen blowing. Two cycles of blowing were performed at intervals of 5 min. The polymer is consolidated for about four hours at ambient conditions, after which the polymerization is completed overnight at 353 K. After complete consolidation, the coated substrates were heated to 823 K in an inert atmosphere (argon) for 2 hr. These conditions were effective to convert the polymeric coating into carbon. This procedure resulted in samples having a carbon load of ca. 13 wt%. The obtained carbon coated monoliths were activated in a quartz reactor placed in a horizontal tubular furnace. The monoliths were therefore heated in a 10% O<sub>2</sub> in Ar mixture up to 603 K, maintained at this temperature for 1.5 hr and subsequently cooled under Ar to room temperature. Afterwards the monoliths were placed in the opposite direction in the reactor (horizontal flip) and the above-mentioned activation step was repeated. This procedure was followed to avoid burn-off profiles over the length of the monoliths. Exchangeable carboxylic acid groups were introduced by functionalization (3-7.5 wt% NaOCl or 1 M HNO<sub>3</sub> for different periods of time). Platinum was applied by cationic exchange with Pt(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub> in diluted NH<sub>3</sub> (aq) for 8 hr, followed by washing and drying. The catalysts were reduced in hydrogen at 573 K for 2 hr and afterwards passivated by a mixture of 1% O<sub>2</sub> in nitrogen for 12 hr.

### 2.2 Nomenclature of used samples

The preparation procedure and nomenclature of the samples used in this study is explained next:

Support C. A carbon coated monolithic support prepared by carbonization of a furfuryl alcohol/pyrrole polymer in Ar at 823 K for 2 hr.

Support C-PEG5000. Similar to support C, but now 90 ml of PEG-5000 was added to the polymerization mixture.

Support C2. Prepared by activation of support C in 10% O<sub>2</sub> in Ar at 603 K for 3 hr.

Support C3. Prepared by functionalization of support C2 in 7.5 wt% NaOCl for 5 min.

Support C3O<sub>x</sub>Cl<sub>y</sub>. Prepared from support C2 by functionalization in 3 wt% NaOCl for *x* hr and washing in 1.25 M HCl for *y* hr.

Support C3HN. Prepared from support C2 by functionalization in 1 M HNO<sub>3</sub> for 0.5 hr.

Catalyst Pt/C. Prepared by ion exchange of Pt(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub> from an ammoniacal solution onto support C3 followed by reduction in hydrogen at 573 K for 2 hours, after which the catalyst was passivated.

Catalyst Pt/C3HN. Similar to catalyst Pt/C, but now ion exchange was performed onto support C3HN.

### 2.3 Catalyst characterization

2.3.1 *Texture*. Prior to analysis the samples were degassed at 623 K for 16 hr.

The CO<sub>2</sub> adsorption isotherm at 273 K has been measured with the Quantachrome NOVA 1200. The micropore volume and surface area were calculated using the Dubinin-Raduskevich (DR) equation. Nitrogen physisorption measurements were performed at 77 K on a Quantachrome Autosorb 6B. The specific surface area of the samples was determined from the adsorption isotherms by the BET-theory. Calculations were performed in the relative pressure range 0.01-0.10 following standard ASTM D-4365, which is applicable to micro-porous materials. Using this technique pore diameters in the region of 1.5-200 nm could be analyzed. The specific surface area and pore volume of each sample was calculated based on the carbon content, rather than on the total mass, since the sample contained about 87 wt% ceramic support which showed no evidence of micro- or mesoporosity.

Mercury porosimetry data were obtained using CE Instruments PASCAL 140/440, which is capable of measuring pore diameters in the range of 4 nm-100 μm.

2.3.2 *Surface chemistry*. The surface chemistry of the carbon supports was studied by TPD-MS and DRIFT.

Temperature Programmed Decomposition-Mass Spectroscopy (TPD-MS) measurements were performed in a conventional flow apparatus using a quartz microreactor and He as carrier gas flowing at 50 STP cm<sup>3</sup> min<sup>-1</sup>. About 200 mg of sample was heated with a rate of 10 K min<sup>-1</sup> up to 1273 K. The desorption processes of gaseous species from the sample were monitored by a quadrupole mass spectrometer (Balzers) connected on-line with the reactor. Mass spectra were recorded in multiple ion detection (MID) mode using a channeltron detector. Evolved CO and CO<sub>2</sub> were calibrated by a method described by Wang and McEnaney [17] using the thermal decompositions of calcium carbonate and calcium oxalate.

Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectra were recorded on a Nicolet Magna 550 FT-IR spectrometer. As the Magna 550 spectrometer is a single beam apparatus, DRIFT spectra were recorded against a background spectrum recorded for a sample cup filled with KBr. The spectra were obtained by collection of 256 scans at 8 cm<sup>-1</sup> resolution and are displayed in absorption reflectance units. From the spectra of the carbon coated monoliths the spectrum of cordierite was subtracted to show the carbon functionalities.

2.3.3 *Carbon coverage*. The carbon coverage was studied by SEM and leaching tests.

The Scanning Electron Microscopy (SEM)-analysis was conducted using a Philips SEM XL20 equipped with a SED detector for secondary and back-scattered electrons. The magnification range is 10 to 400.000x. For the examination of the coverage of carbon, coating thickness and the porosity, the samples were mounted on an aluminum stub and, in some cases, sputtered with gold to provide sufficient electrical conductivity. The images were obtained at 15 kV.

Leaching tests were performed by immersing the carbon coated monoliths and the bare cordierite in HCl solutions for 18 hr at room temperature. To study the influence of pH the molarity of the HCl solution was varied between 0.001 M and 1 M HCl. The amount of solution was fixed to obtain a weight ratio monolith/HCl of 1:25. After 18 hr the monoliths were withdrawn from the solution and the liquid was filtered. The concentration of the cations Si, Mg and Al was analyzed by ICP-OES performed on a Perkin-Elmer Optima 3000DV.

2.3.4 *Platinum surface area and dispersion*. The active platinum surface area and dispersion of the catalysts were determined by volumetric CO chemisorption. The pre-treatment as well as the analysis was performed on the Quantachrome Autosorb-1C. Prior to analysis the samples were dried in vacuum at 393 K. After drying the passivated samples were reduced in hydrogen for 0.5 hr at 303 K and evacuated at 303 K for 1 hr. After cooling down in vacuum the CO adsorption isotherms were measured at 303 K. The isotherm was measured twice using an evacuation step at analysis temperature in between to correct for weakly adsorbed hydrogen. The difference between both isotherms represents the monolayer volume. This monolayer volume is used to calculate the active metal surface area assuming a Pt:CO stoichiometry of 1:1.

### 3. Results and discussion

The preparation and performance of carbon coated monolithic catalysts are dependent on the texture of the catalysts, carbon- and metal load, metal dispersion, thickness of the coating layer and the carbon surface chemistry. These characteristics have been described in more detail below for the samples prepared in this study.

#### 3.1 Texture

The texture of the carbon coated monolithic supports was studied by N<sub>2</sub>-adsorption, CO<sub>2</sub>-adsorption and mercury porosimetry. For none of the samples the hysteresis loops of the N<sub>2</sub>-isotherms were closed at low pressure. This is caused by the so-called 'activated diffusion effect', and results in an underestimation of the porosity. The carbonized carbon coated monolith (support C) exhibits a micro- macroporous structure (Table 1). At this stage the carbon has a very low specific surface area and the texture was further developed by partial oxidation in diluted air. Air activation of the carbonized material (support C2) gives rise to an increase of the N<sub>2</sub>-specific surface area, from 241 m<sup>2</sup>/g<sub>carbon</sub> for the non-activated sample to 390 m<sup>2</sup>/g<sub>carbon</sub> for the material activated at 603 K, but did not develop microporosity, since the CO<sub>2</sub> adsorption hardly changed. The areas are low compared to those of activated carbons (up to 1500-2000 m<sup>2</sup>/g<sub>carbon</sub>). Apparently, at the selected temperature the formed C-O complexes can hardly be removed from the surface, which results in low burn-off levels (ca. 10 wt%). The porosity of the coating can be improved by applying more harsh activation conditions (higher temperatures, longer dwell times), but has the drawback that the carbon coating will be damaged. Another possibility to improve the porosity is by adding a pore-forming agent to the polymerization mixture. The use of PEG-5000 resulted in a large increase of the mesopore volume with pores in the region of 2-10 nm, while no formation of macropores was observed.

None of the carbon coated monoliths show an increase in the Hg intrusion volume when compared with the bare cordierite. The carbon coating is therefore expected to be located on the inside of the cordierite macropore walls as is confirmed by SEM-analysis.

#### 3.2 Surface chemistry

3.2.1 *TPD-MS*. In the preparation of platinum on carbon coated ceramic monoliths different steps can be discerned, i.e. carbonization, activation, functionalization and cationic exchange. TPD experiments were used to characterize the surface oxygen groups formed during these different steps. Upon heating these functional groups decompose and evolve as CO and CO<sub>2</sub>. CO<sub>2</sub> appears at lower temperatures and is ascribed to the decomposition of carboxylic, anhydride and/or lactone groups: acidic

groups where C is bonded to two oxygen atoms. On the other hand, CO desorption occurs at higher temperatures from the decomposition of different types of surface oxygen groups, i.e. phenolic, carbonyl, quinone, ether and pyrone groups: weakly acidic, neutral and basic groups, respectively, where C is bonded to one O atom. Cyclic anhydrides or carboxylic acids produce CO<sub>2</sub> and CO under thermal decomposition [18-21].

The comparison of TPD spectra of carbons C, C2, C3 and Pt/C, presented in Figure 1, shows the effect of the different steps in the preparation of Pt/C-catalysts on the carbon surface chemistry. Though the shape of all TPD spectra is similar (CO<sub>2</sub> evolution below 1000 K and CO evolution above 673 K) the quantity of the evolved gases is different (Table 2). Furthermore, it can be seen that CO evolution from all supports is not complete at 1273 K, the maximum temperature with a dwell time of one hour.

The TPD pattern of sample C is typical of a nonoxidized carbonaceous material with a very low oxygen content. The CO/CO<sub>2</sub> ratio (Table 2) is quite high indicating that the surface of this carbon has a neutral or weakly basic character and suggests that the CO-generating groups have a weakly acidic, neutral or basic character such as phenolic, carbonyl, quinone or pyrone groups [19].

When sample C is activated with 10% O<sub>2</sub> in Ar there is a change in its surface chemical nature and a larger amount of oxygen surface complexes is formed. Figure 1 shows that CO<sub>2</sub>-generating groups are decomposed at low temperatures with the maximum rate at around 823 K. The CO<sub>2</sub> profile, below this temperature, presents a shoulder or tail down to 373 K indicative of the occurrence of different complexes and/or the same oxygen complex existing on energetically different sites. It has been shown that carboxyl anhydride groups are more stable than carboxyl acid groups and, therefore, they evolve as CO and CO<sub>2</sub> above 600 K [20,22]. The CO profile presents a maximum at around 900 K and another peak at around 1273 K (temperature of the maximum rate of this second peak cannot be determined since the evolution of CO was not complete at 1273 K). The occurrence of these two peaks presumably results from the decomposition of different types of CO complexes.

Data from Table 2 show that the NaOCl treatment of sample C2 to obtain sample C3 gives an increase in the number of CO<sub>2</sub>-generating groups, while the number of CO-generating groups remains practically unaltered which causes the CO/CO<sub>2</sub> ratio to decrease.

The TPD profile of the cationic exchanged sample is quite distinct from the pretreated supports. The number of CO<sub>2</sub>-generating groups has decreased dramatically compared to

support C3, whilst there is a slight increase in the number of CO complexes. The lower amount of desorbed CO<sub>2</sub> suggests that upon interaction of Pt with the acidic groups, decomposition of surface oxygen complexes occurs during the reduction treatment at 573 K. Furthermore, the CO<sub>2</sub>-profile has shifted to lower temperature by about 100 K. These observations imply that the catalyst preparation step and the presence of platinum may appreciably modify the surface chemistry of the cationic exchanged samples in contrast to what is stated in literature [21].

The functionalization step, as reported for support C3, is not well controlled due to the high concentration of NaOCl and the short oxidation time. Therefore the concentration of NaOCl was lowered to 3 wt% and the oxidation time was extended. Furthermore, a washing step in 1.25 N HCl for 0.5 hr was introduced to remove the excess of sodium hypochlorite from the surface of the carbon. Removal of sodium is necessary since Na can catalyze undesired reactions, alter the sintering resistance of the supported metal or act as catalyst poison and thus adversely affect catalyst performance.

Upon increasing the oxidation time only a slight increase in the number of acidic groups was found while the number of CO-generating groups decreased (Table 2).

The washing period of 0.5 hr in 1.25 N HCl proved to be insufficient, since after TPD experiments the presence of a white salt (possibly sodium carbonate) was observed on visual inspection of the quartz reactor. Therefore the washing time was increased.

Data from Table 2 show that the treatment in HCl for  $\gamma$  hr gives an increase in the number of CO-generating groups, while the number of CO<sub>2</sub>-generating groups decreases. This result is rather surprising since HCl is no oxidizing agent. According to Wang and Lu [23] the change in surface chemistry upon treatment in HCl may be attributed to the removal of inorganic compounds (Na) leaving sites on the carbon surface which can chemisorb oxygen in air at room temperature, which would result in more oxygen surface complexes.

Even the extension of the washing period did not result in the complete disappearance of the sodium from the carbon surface (after TPD experiments still some white salt could be observed on the reactor, although less). Therefore it was compared with functionalization in 1 M HNO<sub>3</sub> for half an hour. Compared to C3O<sub>x</sub> an increase in the number of CO-generating groups can be observed for C3HN (Figure 2), while the number of CO<sub>2</sub>-generating groups remains practically unaltered. The higher peak intensity in the CO<sub>2</sub>-profile of C3O<sub>x</sub> at 473-673 K indicates that functionalization in NaOCl creates more carboxylic

groups, while treatment in HNO<sub>3</sub> creates more anhydride groups (> 600 K) [24].

**3.2.2 DRIFT.** The FT-IR spectra of the carbonized carbon C, activated carbon C2 and functionalized carbon C3HN are presented in Figure 3. Band assignments for the spectrum of support C indicate that the carbonized carbon contains a number of atomic groups and structures (OH, CH<sub>2</sub>, C=O, C-O-C, and so on). A very broad band at wavenumbers lower than 1850 cm<sup>-1</sup> is detected. It originates from the overlapping of various individual absorption bands. In this spectrum, the broad peak at 1149 cm<sup>-1</sup> can be assigned to C-O stretching vibrations in phenolic groups. The band at 1261 cm<sup>-1</sup> can be assigned to (C-O) stretch vibrations in ether-like functionalities. Specifically, these spectral features can be associated with the asymmetric stretching vibration mode of C-O-C in single graphitic sheets and between two of such sheets, respectively. The band at 1368 cm<sup>-1</sup> is characteristic for methyl groups. Also, the 1400 cm<sup>-1</sup> region gives some idea of the relative abundance of CH<sub>2</sub> and CH<sub>3</sub> groups [25,26]. The band at 1620 cm<sup>-1</sup> is a characteristic peak for carbonaceous materials and is ascribed to quinone-type carbonyl oxygen conjugated with the carbon basal plane [27].

Activation of the carbonized support greatly increases the absorption of infrared radiation within the 950-2000 cm<sup>-1</sup> range. An additional band is observed at 1714 cm<sup>-1</sup> in the FT-IR-spectrum of support C2. The 1714 cm<sup>-1</sup> band is characteristic of stretching vibrations of carbonyl groups C=O in carboxylic acid groups and lactones. The carboxylic acid groups should also have an absorption band at ~3500 cm<sup>-1</sup>. However, the intense broad peak in the 3500 cm<sup>-1</sup> region is not an unequivocal identification because of the possibility of adsorbed water present in the sample. The broad band at 1149 cm<sup>-1</sup> may have contributions from both C-O stretching and O-H bending modes in phenolic, carboxylic acid groups [27].

When the spectrum of the functionalized carbon (C3HN) is compared to that of C2, it can be deduced that functionalization does not produce strong changes in the chemical nature of the material. No additional bands appear in the spectrum of C3HN, while the absorption of infrared radiation is slightly increased within the 950-2000 cm<sup>-1</sup> range indicating a higher amount of oxygen surface complexes as is also witnessed by TPD-MS.

### 3.3 Carbon coverage

**3.3.1 SEM.** SEM analysis showed that the carbon is located primarily in the macroporous structure of the cordierite with only a thin layer on the external surface of the support. The application of a coating therefore hardly affects the geometric surface properties of the monolithic

support (Figure 4a). In case of square cells, there is carbon accumulation in the corners of the cells. A more uniform thickness of the coating layer can be obtained when the corners of the cells are more rounded (Figure 4b). Details of carbon inclusions are given in Figure 4c. The penetration of the carbon precursor in the porous network of the cordierite creates a coating that is physically interlocked with the interconnecting porosity of the substrate. This results in an adherent coating which is highly resistant to flaking. From Figure 4d it can be seen that cracks are formed in the thicker corner region upon carbonization due to shrinkage of the polymer. The structure contracts because of the removal of functional groups and rearrangement of atoms.

**3.3.2 Leaching.** The coating efficiency of the cordierite has also been investigated by leaching. Cordierite is susceptible to chemical attack by acids, like sulfuric acid. This reaction is characterized by the decomposition of the original structure and the formation of salts and a silica gel [28]. In this study the use of HCl was preferred over other mineral acids, like HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>, since HCl is not an oxidizing agent and therefore will not affect the properties of the carbon coating.

Contacting the bare cordierite with a 0.001 M HCl solution resulted in negligible leaching. The reactivity was enhanced by using a 1 M HCl solution. Conversion of the concentration of cations (Si, Mg, Al) in the leaching solution to weight loss of cations from the cordierite resulted in the data in Figure 5. Especially magnesium and aluminum species are removed from the cordierite. The obtained total weight loss is low compared to the data reported in literature, which vary from 7-32 wt% [29,30]. However, in those studies hot acid solutions (368 K) were used, which results in a higher leaching rate.

The application of a carbon coating increases the resistance to leaching. However, all coated samples still show some leaching indicating that carbon coverage is not complete. Improvement of the presented preparation procedure is thus required. A possibility to increase the coverage of carbon would be repeated coating with intermediate carbonization. A drawback of this method will be that part of the formed porous structure will be filled up as well with fresh polymer. If leaching is an issue the use of another type of substrate is recommended, for example mullite instead of cordierite.

#### 3.4 Catalyst characterization

The platinum catalyst, Pt/C3HN, prepared by cationic-exchange, contained 0.75 wt% metal. Per unit carbon mass the platinum content comes to 5.2 wt%. The active platinum surface area was determined by volumetric CO chemisorption and was calculated to be 0.80 m<sup>2</sup>/g<sub>sample</sub>.

This corresponds with an average metal particle size of 2.6 nm and a metal dispersion of 43%. The high metal dispersion is attributed to the selective exchange of the cations with the acidic (carboxylic) groups of the support and to the stabilizing interaction of the particles with the functional groups [31].

## 4. Conclusions

Carbon coated monoliths have been prepared by dipcoating ceramic monoliths in a partially polymerized mixture of furfuryl alcohol and pyrrole. SEM-analysis showed that the carbon precursor penetrates in the porous network of the cordierite, creating a coating that is physically interlocked with the substrate. Upon carbonization, the polymer coating contracts causing cracks in the corner region of the monolithic channels. The coating reduces leaching, but incomplete coverage of the structure makes these cordierite supports unsuitable as carbon catalyst support material in strongly acidic and basic media.

Mild activation conditions were applied in order to prevent damage of the carbon coating. At the selected temperature (603 K), large amounts of carboxylic acids and quinone-type of structures were formed while hardly any carbon removal took place. The resulting coatings have unfavourable textural properties as catalyst support. The porosity of the carbon can be improved by the addition of a pore-forming agent (PEG-5000) to the carbon yielding precursors. This results in an increase of the specific surface area as measured for the carbonized samples, from 241 m<sup>2</sup>/g<sub>carbon</sub> for the non-PEG sample to 690 m<sup>2</sup>/g<sub>carbon</sub> for the material treated with PEG-5000. The pore volume is increased from 0.14 to 0.75 cm<sup>3</sup>/g<sub>carbon</sub>, while the latter sample has pores in the region of 2-10 nm.

Upon functionalization the number of oxygen surface complexes increased. Treatment in 1 M HNO<sub>3</sub> generated a more intense oxidation than in 3 wt% NaOCl, resulting in the evolution of larger amounts of CO as observed by TPD-MS.

The selective exchange of the [Pt(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> cations with the acidic (carboxylic) groups of the functionalized support, resulted in a high metal loading (5.2 wt% Pt/C) and dispersion (43%) for the Pt/C/cordierite catalysts.

## 5. Acknowledgement

This work was supported by the European Union under contract number BRPR-CT97-0561. Corning Inc. (Corning, USA) is acknowledged for the supply of ceramic monolithic substrates. Dr. Guido Mul is

acknowledged for his help with the interpretation of the FT-IR data.

## 6. References

1. Radovic, L.R. and Sudhakar, C., Carbon as a catalyst support: Production, properties and applications, in: Introduction to Carbon Technologies, Marsh, H., Heintz, E.A., and Rodríguez-Reinoso, F. (Eds.), Introduction to Carbon Technologies, 1997, 103 - 165.
2. Rodríguez-Reinoso, F., Carbon, 36, (1998), 159 - 175.
3. Rodríguez-Reinoso, F., Rodríguez-Ramos, I., Moreno-Castilla, C., Guerrero-Ruiz, A., and López-González, J.D., J.Catal., 99, (1986), 171 - 183.
4. Tennison, S.R., Appl.Catal.A: Gen., 173, (1998), 289 - 311.
5. Kapteijn, F., Heiszwolf, J.J., Nijhuis, T.A., and Moulijn, J.A., CATTECH, 3, (1999), 24 - 41.
6. Gadkaree, K.P. and Jaroniec, M., Carbon, 38, (2000), 983 - 993.
7. Vergunst, Th., Linders, M.J.G., Kapteijn, F., and Moulijn, J.A., Catalysis Reviews, (2001), in press.
8. Gadkaree, K.P., Carbon, 36, (1998), 981 - 989.
9. DeLiso, E.M., Gadkaree, K. P., Mach, J. F., and Streicher, K. P., US 5,451,444, (1995).
10. Gadkaree, K.P., US 5,487,917, (1996).
11. Valdés-Solís, T., Marbán, G., and Fuertes, A.B., Microporous and Mesoporous Materials, 43, (2001), 113 - 126.
12. Vergunst, Th., Kapteijn, F., and Moulijn, J.A., Carbon coating of ceramic monolithic substrates, in: Preparation of catalysts VII, Studies in Surf.Sci.and Catalysis, Ed 118, 1998, 175 - 183.
13. Vergunst, Th., Kapteijn, F., and Moulijn, J.A., Catal.Today, (2001), in press.
14. Crezee, E., Barendregt, A., Kapteijn, F., and Moulijn, J.A., Catal.Today, submitted.
15. Besson, M., Blackburn, A., Claverie, S., Gallezot, P., Kozynchenko, O., and Tennison, S.R., 5th International Symposium on Heterogeneous Catalysis and Fine Chemicals, Lyon, (1999), P46.
16. Hucke, E.E., US 3,859,421, (1975).
17. Wang, J. and McEnaney, B., Thermochemica Acta, 190, (1991), 143 - 153.
18. De la Puente, G., Pis, J.J., Menéndez, J.A., and Grange, P., Journal of Analytical and Applied Pyrolysis, 43, (1997), 125 - 138.
19. Moreno-Castilla, C., Ferro-García, M.A., Rivera-Utrilla, J., and Joly, J.P., Energy & Fuels, 8, (1994), 1233 - 1237.
20. Román-Martínez, M.C., Cazorla-Amorós, D., Linares-Solano, A., and Salinas-Martínez de Lecea, C., Carbon, 31, (1993), 895 - 902.
21. Román-Martínez, M.C., Cazorla-Amorós, D., Linares-Solano, A., and Salinas-Martínez de Lecea, C., Current Topics in Catalysis, 1, (1997), 17 - 46.
22. Otake, Y. and Jenkins, R.G., Carbon, 31, (1993), 109 - 121.
23. Wang, S. and Lu, G.Q.M., Carbon, 36, (1998), 283 - 292.
24. Pereira, M.F.R., Órfão, J.J.M., and Figueiredo, J.L., Appl.Catal.A: Gen., 184, (1999), 153 - 160.
25. Gómez-Serrano, V., Carbon, 37, (1999), 1517 - 1528.
26. Mul, G., Catalytic diesel exhaust purification, A DRIFT spectroscopic and mechanical study of soot oxidation, Ph.D. Thesis, Delft University of Technology, Delft, (1997).
27. Jia, Y.F. and Thomas, K.M., Langmuir, 16, (2000), 1114 - 1122.
28. Day, J.P., Trans.ASME, 101, (1979), 270 - 274.
29. Lachman, I.M. and Patil, M. D., US 4,800,187, (1989).
30. Elmer, T.H., US 3,958,058, (1976).
31. Gallezot, P., Laurain, N., and Isnard, P., Appl.Catal.B:Env., 9, (1996), L11 - L17.

Table 1. Textural properties of supports determined by physical adsorption, N<sub>2</sub> at 77 K and CO<sub>2</sub> at 273 K, and mercury porosimetry.

Sample	Carbon load [wt%]	N <sub>2</sub> physisorption		CO <sub>2</sub> physisorption		Hg intrusion
		$S_{\text{BET}}^{\text{N}_2}$ [m <sup>2</sup> g <sub>carbon</sub> <sup>-1</sup> ]	$V_{\text{pore}}^{\text{N}_2}$ [cm <sup>3</sup> g <sub>carbon</sub> <sup>-1</sup> ]	$S_{\text{DR, micro}}^{\text{CO}_2}$ [m <sup>2</sup> g <sub>carbon</sub> <sup>-1</sup> ]	$V_{\text{DR, micro}}^{\text{CO}_2}$ [cm <sup>3</sup> g <sub>carbon</sub> <sup>-1</sup> ]	$V_{\text{intrusion}}^{\text{Hg}}$ [cm <sup>3</sup> g <sub>sample</sub> <sup>-1</sup> ]
cordierite	-					0.22
C	13.7	241	0.14	527	0.19	0.17
C-PEG5000	11.6	690	0.75	449	0.17	0.17
C2	13.6	390	0.19	471	0.17	0.15
C3HN	13.0	401	0.19	501	0.18	0.15

Table 2. Total amounts of CO and CO<sub>2</sub> evolved by the different pre-treatments of carbon coated monolithic supports.

Sample	Amount desorbed [mmol/g <sub>carbon</sub> ]		CO/CO <sub>2</sub> -ratio	O [wt%]
	CO	CO <sub>2</sub>		
C	1.2	0.39	3.2	3.2
C2	2.9	1.3	2.2	8.8
C3	2.6	1.9	1.4	10.3
Pt/C	2.9	1.0	2.9	7.8
C3O <sub>1/2</sub> Cl <sub>1/2</sub>	3.4	1.8	1.9	11.1
C3O <sub>8</sub> Cl <sub>1/2</sub>	3.0	1.9	1.6	10.7
C3O <sub>27</sub> Cl <sub>1/2</sub>	2.9	2.0	1.4	11.2
C3O <sub>1/2</sub>	2.7	2.5	1.1	12.1
C3O <sub>1/2</sub> Cl <sub>1/2</sub>	3.4	1.8	1.9	11.1
C3O <sub>1/2</sub> Cl <sub>24</sub>	3.7	2.1	1.8	12.6
C3HN	4.6	2.4	1.9	15.2

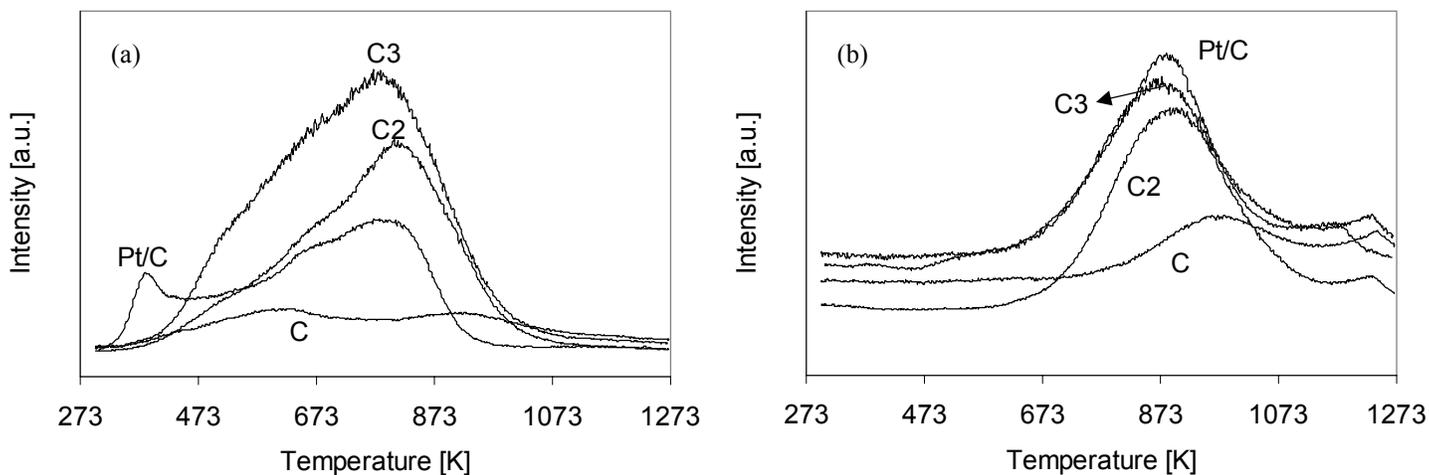


Figure 1. TPD spectra of supports C, C2, C3 and catalyst Pt/C: (a) CO<sub>2</sub> desorption, (b) CO desorption.

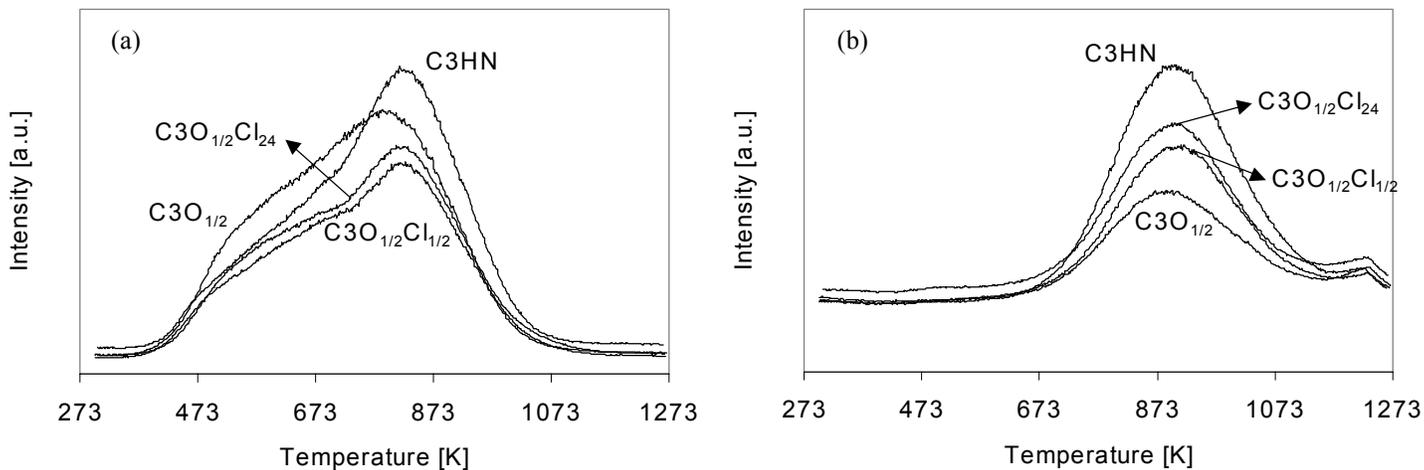


Figure 2. Effects of acidic treatments on the surface chemistry of carbon coated monolithic supports; (a) CO<sub>2</sub> desorption, (b) CO desorption.

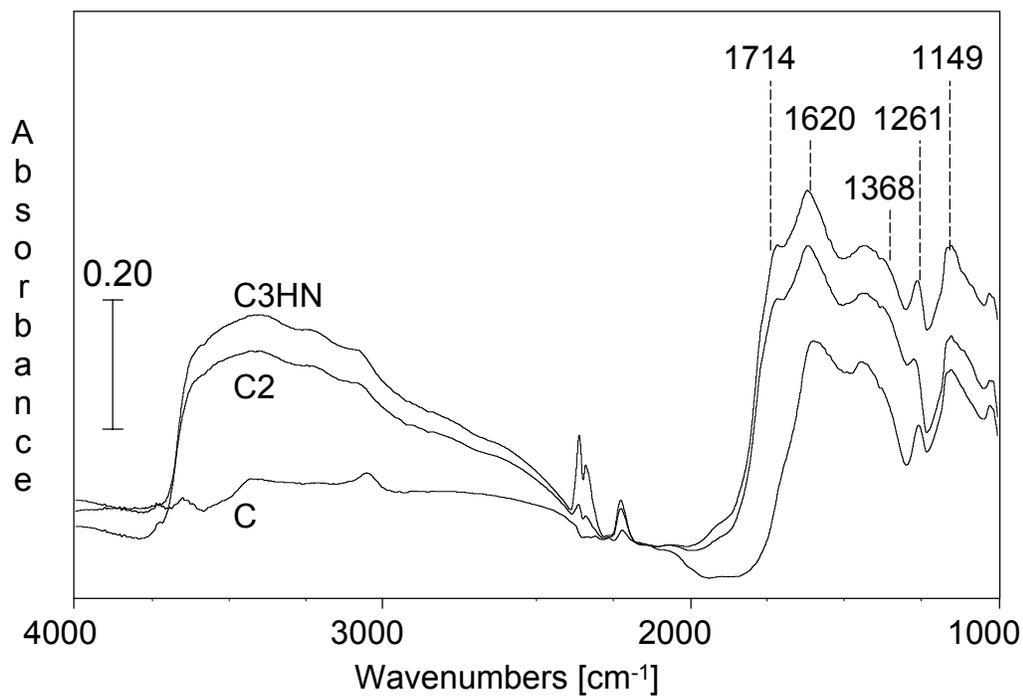


Figure 3. DRIFT spectra of supports C, C2 and C3HN.

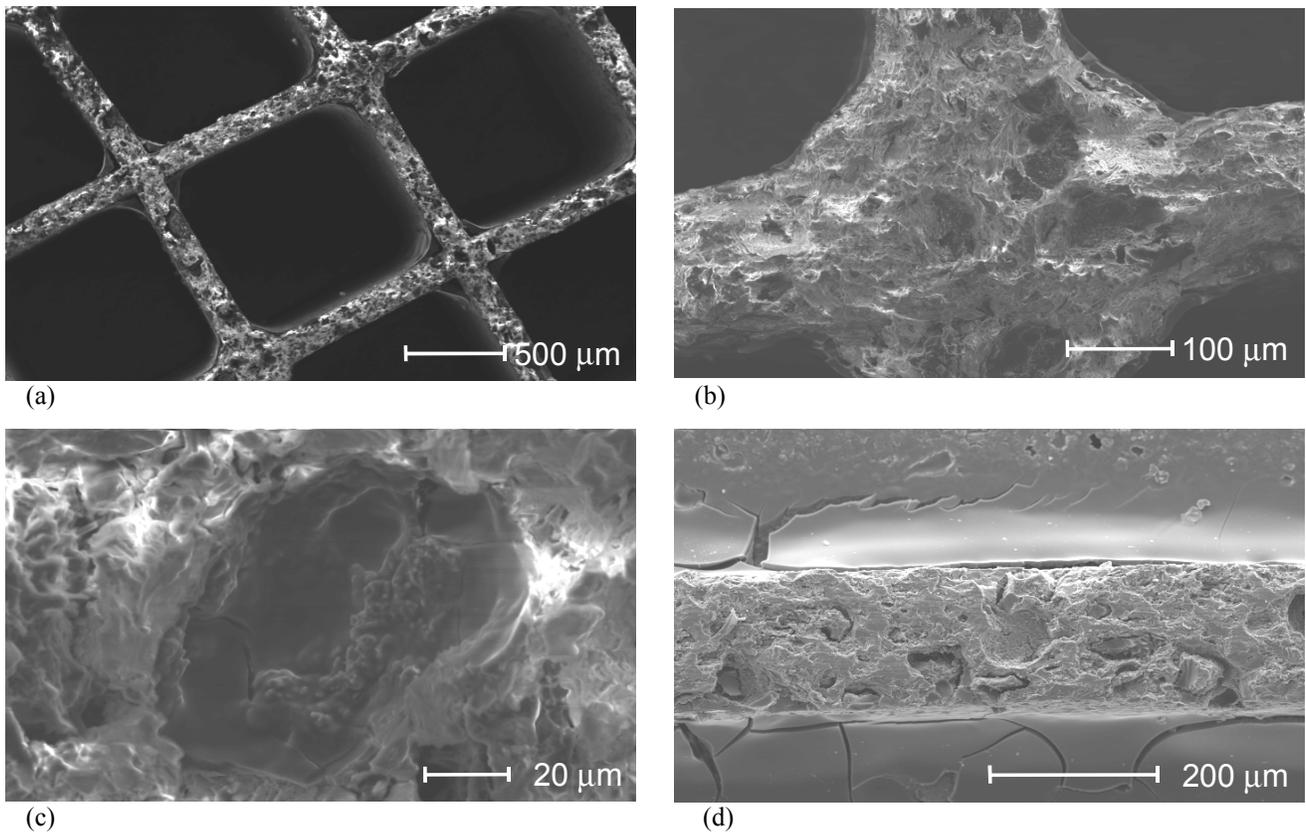


Figure 4. SEM micrographs of carbon coated monoliths: (a) cross-section; (b) detail of the thickness of the coating layer; (c) carbon inclusions in the cordierite matrix; (d) transversal section of monolithic walls. Photographs are backscattered electron images, except for the bottom right one which is a secondary electron image (gold sputtered).

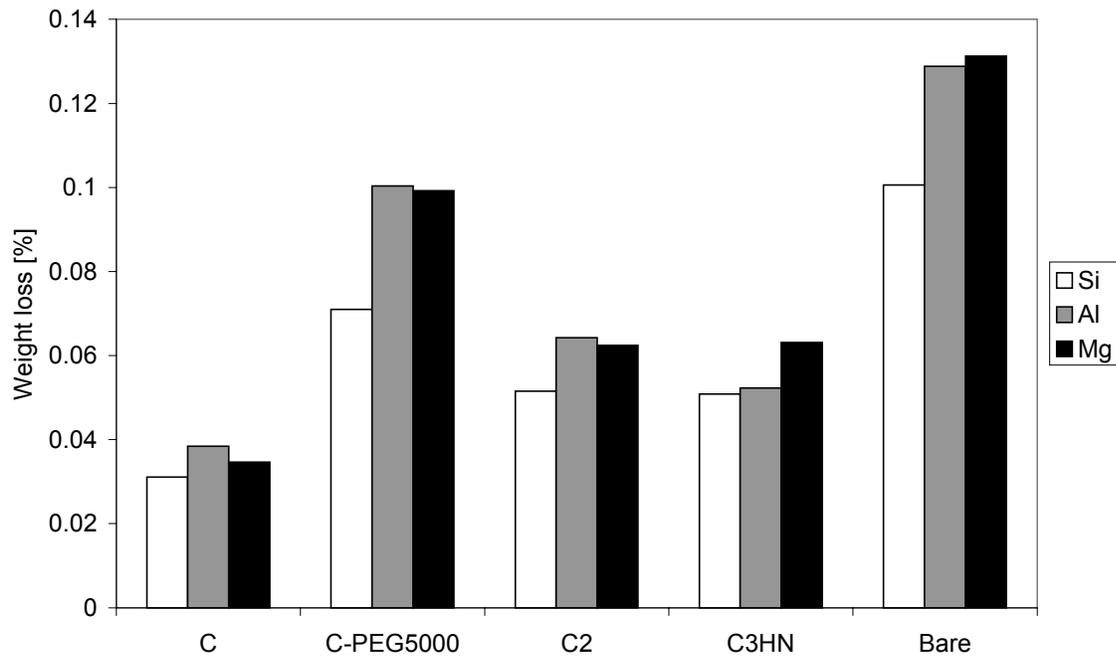


Figure 5. Weight loss of cations from the cordierite for the different samples after leaching.