STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLVIII, 2, 2003

# PREPARARATION AND POROUS STRUCTURE DETERMINATION OF RESORCINOL–FORMALDEHYDE AND CARBON AEROGELS

**VIRGINIA DANCIU[a], L.C. COTEŢ[a], VERONICA COŞOVEANU[a], P. MARGINEAN[b]**

[a] *"Babeş-Bolyai" University, Faculty of Chemistry and Chemical Engineering,*
*Electrochemical Research Laboratory, Arany Janos St., 11, Cluj-Napoca*
[b] *National Institute for Research and Development of Isotopic and Molecular*
*Technologies, Donath St., 71-103, Cluj-Napoca*

**ABSTRACT**. Carbon aerogels are special porous materials consisting of interconnected nanometer-sized particles with small interstitial pores, this structure determining a very high surface area and a high electrical conductivity. These aerogels have found use as electrode materials in several electrochemical devices, most notably, aerocapacitors and electrosorption processes. In order to obtain a matrix for sensor development we studied the preparation and morphology of the C-aerogels. Carbon aerogels were prepared by the sol-gel polycondensation of resorcinol (R) with formaldehyde (F) in a slightly basic aqueous solution ($Na_2CO_3$) followed by supercritical drying with $CO_2$ and pyrolysis of obtained resorcinol-formaldehyde (RF) aerogels in an inert atmosphere. The porous structures of the resorcinol-formaldehyde (RF) and carbon (C) aerogels were estimated by krypton adsorption. It was found that the mesopore structure (pore and distribution) strongly depends on the sol-gel reaction, drying and pyrolysis conditions.

**KEYWORDS**: Resorcinol-formaldehyde aerogel, Carbon aerogel, sol-gel poly-condensation, supercritical drying, porosity

## 1. INTRODUCTION

The preparation of aerogels starts with the controlled conversion of sol into gel, such as the growth of clusters or polymer chains from a chemical solution, the cross-linking of the primary entities, and the formation of a network. A supercritical drying allows the liquid to drain from the delicate gel structure without any collapse or shrinkage caused by surface tension of the liquid at evaporation [1-3].

Pekala *et al.* prepared the first organic aerogels from the polycondensation of resorcinol (1,3-dihydroxybenzene) with formaldehyde, followed by supercritical drying. The authors have experimentally elucidated the influence of the resorcinol / catalyst mole ratio on the porous structure of RF aerogels. Subsequent pyrolysis of these materials at an elevated temperature ($1050^{O}C$) in an inert atmosphere produces carbon aerogels [4-7].

Carbon aerogels are unique porous materials consisting of interconnected nanometer – sized particles (3 – 30nm) with small interstitial pores (< 50nm). The aerogel chemical composition, microstructure and physical properties can be controlled at the nanometer scale, giving rise to unique optical, thermal, acoustic, mechanical and electrical properties. Among their many applications, carbon aerogels are used as electrode materials in several electrochemical devices, most notably, aerocapacitors and electrosorbtion processes [7-10]. Carbon aerogels provide an almost ideal electrode material because of their high electrical conductivity (10 - 100 S/cm), high surface areas (400 - 1000 $m^2/g$), interconnected and open pore structure with controllable pore size (30 - 500Å).

In order to obtain a matrix for sensor development, RF and carbon aerogels are prepared by sol-gel method using a SAMDRI-PVT-3D supercritical dryer. The influence of the amount of reactants, diluent and basic catalyst used in the polycondensation and the porous structures are experimentally studied in view to obtain a mesoporous structure of the aerogels.

## 2. EXPERIMENTAL SECTION

### 2.1. Synthesis of RF aquagels

RF aquagels were synthesized by polycondensation of resorcinol with formaldehyde according to Pekala *et al.* [4-8], for **α** to **ε** type of gels, and Tamon *et al.* [11-16], for $\mathbf{D_I}$ to $\mathbf{D_{VII}}$ gels. $Na_2CO_3$ p.a. (Reactivul, Bucuresti) was used as basic catalyst. RF solutions were prepared from resorcinol (MERCK – Schuchardt, for synthesis, >99%), formaldehyde (S.C. REMED PRODIMPEX S.R.L., research grade, 37 wt% formaldehyde stabilized with 8 wt% methanol). The water used as diluent was distilled after ion exchange; its electric resistivity was $\geq 50 \times 10^4$ Ωm and its pH was 5.8. The synthesis conditions are listed in table 1. The (α - ε) RF aquagels were obtained by transferring the resorcinol-formaldehyde mixtures into glass ampoules (10 $cm^3$ capacity), sealed with an methane torch and placed in an oven at 85±3 °C for 7 days. The solutions progressively changed color from clear to yellow, to orange, to deep red as a function of the reaction time. Gel time was a function of the percent solids in the mixture and the catalyst level. Upon completion of the cure cycle, the glass ampoules were removed from the oven and cooled to room temperature. After removal from the ampoules, the RF gels were placed in an agitated bath of 0.125% trifluoracetic acid at 45 °C for 3 days in order to assist the further condensation of hydroxymethyl groups remained in the gels and the increasing in the compressive modulus of the gels.

The ($D_I$ –$D_{VIII}$) RF aquagels were obtained by curing the solutions, put in sealed ampoules, for 1 day at room temperature, 1 day at 50°C and 3 days at 90°C.

**Table 1**

RF aquagels preparation conditions

| **RF type** | **R/F** [mol/mol] | **Solid weight** [%] | **$R/Na_2CO_3$** [mol/mol] | **R/ $H_2O$** [g/$cm^3$] | **$F/Na_2CO_3$** [mol/mol] | **pH** |
|---|---|---|---|---|---|---|
| **α** | 0.500 | 5 | 50 | 0.033 | 100 | 7.37 |
| **β** | 0.500 | 5 | 76.31 | 0.033 | 152.6 | 7.15 |
| **γ** | 0.500 | 5 | 96.66 | 0.033 | 193 | 7.05 |
| **δ** | 0.510 | 4 | 102.12 | 0.033 | 200 | 7.23 |
| **ε** | 0.512 | 3.5 | 107.69 | 0.033 | 210 | 7.35 |
| $\mathbf{D_I}$ | 0.500 | 14.49 | 200 | 0.122 | 400 | 6.67 |
| $\mathbf{D_{II}}$ | 0.500 | 16.19 | 75 | 0.141 | 150 | 6.98 |
| $\mathbf{D_{III}}$ | 0.500 | 16.18 | 100 | 0.141 | 200 | 7.15 |
| $\mathbf{D_{IV}}$ | 0.500 | 16.14 | 200 | 0.141 | 400 | 7.05 |
| $\mathbf{D_V}$ | 0.500 | 27.73 | 200 | 0.325 | 400 | 6.50 |
| $\mathbf{D_{VI}}$ | 0.500 | 43.28 | 200 | 0.930 | 400 | 6.38 |
| $\mathbf{D_{VII}}$ | 0.500 | 43.35 | 200 | 0.926 | 400 | 6.64 |

### 2.2. Preparation of RF aerogels

RF hydrogels were dried under following supercritical conditions. The prepared hydrogels have the structure filled with water. Because water is poorly soluble in $CO_2$, there is danger that water remains in the gel structure after supercritical drying with $CO_2$. For this reason, the gels were immersed in excess of pure acetone or absolute ethanol for >1 week after washing (3 – 4 times) with acetone or ethanol. The hydrogel was placed in the Samdri chamber (20 $cm^3$) with acetone or absolute ethanol. The chamber was then sealed. In order to prevent vaporization of the liquid $CO_2$ the chamber of the SAMDRI-PVT-3D dryer (Tousimis Research Corp., USA) is cooled (with liquid $CO_2$) to near $0^oC$. Then, the liquid carbon dioxide slowly flows (fill rate: 0.43 – 1.3 ml/min) from the siphon – type bomb to the dryer until the pressure reaches about 54.3 atm.

The liquid $CO_2$ flowed throw the chamber at 3 – 5 $cm^3$/min and 0 – $10^oC$ for 4 hours and acetone or ethanol was washed out by $CO_2$. The critical temperature and pressure of $CO_2$ are $31^oC$ and 73.5 atm. Hence, the temperature of the chamber was increased above the critical temperature of $CO_2$ and acetone (ethanol) inside the gel was supercritically extracted at $42^oC$ for 10 - 60 min. After the supercritical extraction, the inside of chamber was slowly depressurized to atmospheric pressure at $42^oC$ for 60 min. and the RF aerogel was obtained. After aging the aerogels at 60 $^oC$ for 2 hours, the porous structure of the aerogels was determined using Kr adsorption at liquid $N_2$ temperature.

### 2.3. Preparation of C aerogels

We prepared carbon aerogels by pyrolysis of RF aerogels in a conventional furnace. $N_2$ flowed through a quartz reactor containing the RF aerogels set in the furnace at 8 $cm^3$/min during the pyrolysis. The furnace was heated to $250^oC$ at $4^oC$/min, maintained at this temperature for 2 hours, then was heated, with the same rate, to $850^o$ and maintained 4 hours. After pyrolysis, the furnace was cooled at the room temperature under its own thermal mass.

### 2.4. Characterization of the RF and C aerogels

The porous structure of RF and C aerogels was determined by Kr adsorption. The adsorption isotherms were obtained using an all glass installation (INCDTIM Cluj-Napoca), at a partial pressure of 0.05-0.35. The samples were preheated for 2h at $60^0C$ before measurement, after their degasification in vacuum. The adsorption and desorption isotherms of Kr were measured at temperature of liquid nitrogen.

The BET surface area ($S_{BET}$), mesopore size distribution and microporosity were determined. The pore size distribution was estimated by applying the Dollimore-Heal method [17] to the measured desorption isotherms and the microporosity (slit width: 0.35-1.0) was evaluated by the t-plot method [18].

## 3. RESULTS AND DISCUSSIONS

### 3.1. Appearance of RF aerogels

RF-aerogels were prepared by changing the mole ratios of resorcinol to basic catalyst (R/C), the ratios of resorcinol to pure water ($R/H_2O$, g/$cm^3$) or the mole ratios of resorcinol to formaldehyde (R/F). Color, transparency and hardness of RF-aquagels depended on $R/Na_2CO_3$, $R/H_2O$ or R/F ratios used in the sol-gel polycondensation. Although the gels were reddish yellow in color and transparent for $50<R/C<200$, they become dark with decreasing $R/Na_2CO_3$.

As for influence of R/$H_2O$ on the aquagel characters, the dark reddish yellow and soft gels were obtained for low R/$H_2O$, and light reddish yellow and hard ones were prepared for high R/$H_2O$.

The gels prepared under the conditions of low R/F had a light color and those prepared for high R/F had a dark color.

### 3.2. Porous structure of RF-aerogels

RF aerogels prepared by supercritical drying with $CO_2$ had the same color as the RF aquagels.

#### 3.2.1. *Effect of R/$Na_2CO_3$ on porous structure of RF-aerogels*

We prepared RF aerogels by changing R/$Na_2CO_3$ ratio under the conditions of R/$H_2O$ = 0.033 (α-ε RF aerogels) and respectively 0.141 ($D_{II}$-$D_{IV}$ RF aerogels) and R/F = 0.5 and we determinated their porous structure by Kr adsorption. Figures 1 and 2 show that for high $Na_2CO_3$ concentration (*i.e.* R/$Na_2CO_3$ = 50), the aerogels have high BET surface areas of *ca* 800 $m^2$/g and large mesopore volumes of *ca* 3.5 $cm^3$/g. For low $Na_2CO_3$ concentration, $S_{BET}$ and $V_{meso}$ decrease with increasing R/$Na_2CO_3$. $S_{micro}$ and $V_{micro}$ are much smaller and have similar R/$Na_2CO_3$ dependencies.

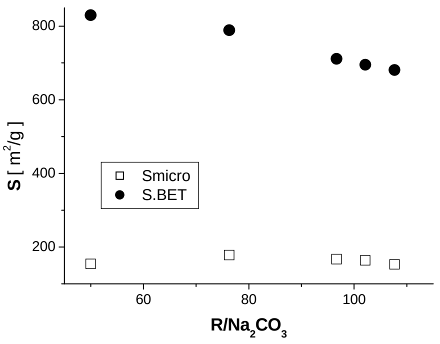

**Figure 1**. *Influence of R/$Na_2CO_3$ on the BET surface area and surface area of micropores of $\alpha,\beta,\gamma,\delta,\varepsilon$ RF aerogels*

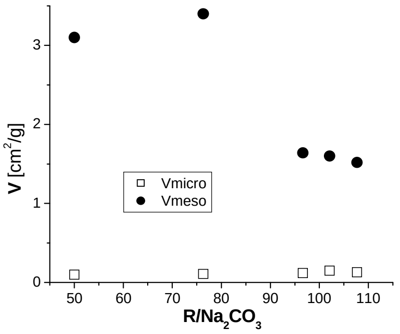

**Figure 2.** *Influence of R/$Na_2CO_3$ on the volume of mesopores ($V_{meso}$) and micropores ($V_{micro}$) of $\alpha$, $\beta$, $\gamma$, $\delta$, $\varepsilon$ RF aerogels*

Figure 3 shows some examples of pore size distribution of RF aerogels. For R/$Na_2CO_3$= 75, the aerogels have monodisperse distribution (a single peak), while for R/$Na_2CO_3$ = 200 a polydisperse distribution (some peaks) was obtained.

#### 3.2.2. *Effect of R/$H_2O$ on porous structure of RF aerogels*

$S_{BET}$ and $S_{micro}$ seem to be independent of R/$H_2O$ as shown figure 4; the results suggest that the particle size constituting the network structure of aerogels is independent of R/$H_2O$.

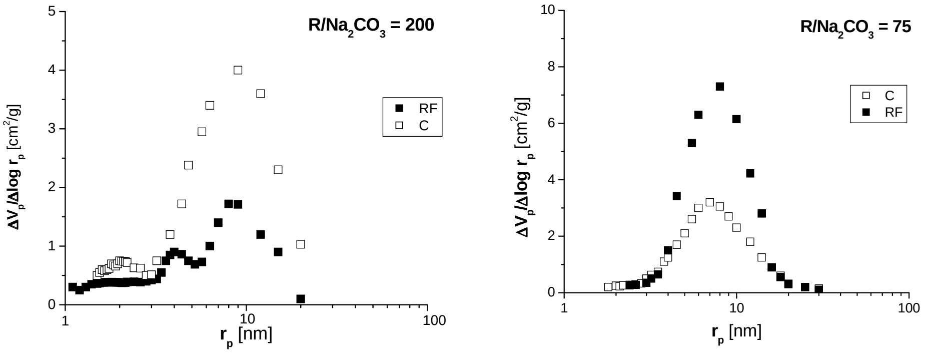

**Figure 3.** *Pore size distribution of RF and C aerogels; R/$H_2O$ = 0.141 and R/F = 0.5*

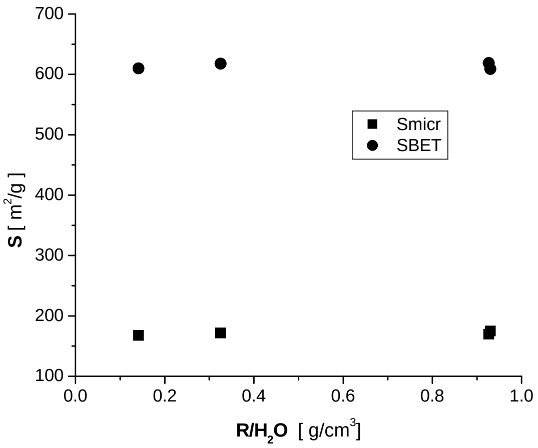

**Figure 4**. *Influence of R/$H_2O$ on the BET surface area and surface area of micropores of RF aerogels*

Figure 5 shows that $V_{meso}$ increases with increasing R/$H_2O$; the aerogels have monodisperse distribution only at R/$H_2O$ = 0.325; in all other studied cases having a polydisperse distribution.

### *3.2.3. Effect of R/F ratio on porous structure of RF aerogels*

For the RF-aerogels prepared under the conditions of R/$Na_2CO_3$=100, R/$H_2O$ = 0.033 and R/F = 0,34 - 0,58 it was observed that $S_{BET}$ was independent of R/F and $V_{meso}$ was larger for R/F > 0.40. $S_{micro}$ and $V_{micro}$ were independent of R/F ratio and smaller than $S_{BET}$ and $V_{meso}$.

### 3.3. Porous structure of C-aerogels

C aerogels were prepared by pyrolysing RF aerogels at 850°C. The aerogels turned from dark reddish yellow and transparent to black and opaque. The porous structure of the carbon aerogels was analyzed by the Kr adsorption method.

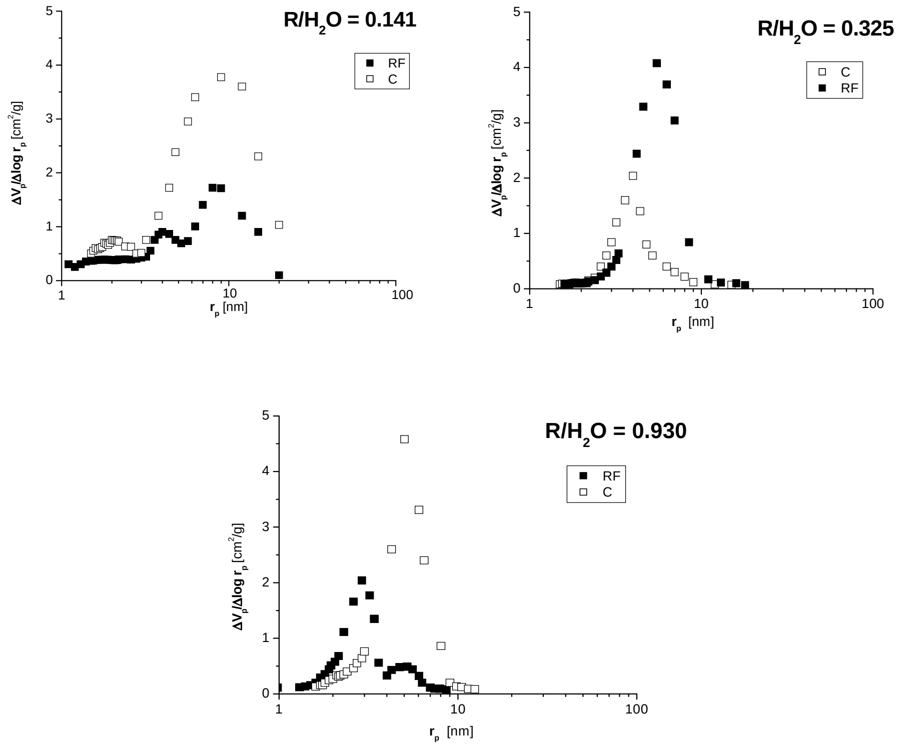

**Figure 5.** *Pore size distribution of RF and C aerogels (R/$Na_2CO_3$ = 200 and R/F = 0.5)*

Table 2 shows that $S_{BET}$ increases for all prepared samples suggesting the formation of micropores. $V_{meso}$ increases or decreases by pyrolysis of RF aerogels. Carbon aerogel prepared from RF aerogel having a monodisperse distribution gives a smaller mesopore volume than the RF aerogel (see fig. 3 - 5).

**Table 2.**

Morphological characteristics of RF and C aerogels

| Conditions of sol-gel polycondensation | Aerogel type | $S_{BET}$ x$10^{-2}$ [$m^2$/g] | $V_{meso}$ [$cm^3$/g] | $r_{peak}$ [nm] | $S_{micro}$ x$10^{-2}$ [$m^2$/g] | $V_{micro}$ x$10^{2}$ [$cm^3$/g] |
|---|---|---|---|---|---|---|
| R/C= 50;<br>R/F=0.5;<br>R/$H_2O$=0,033 | **RF-α**<br>**C-α** | 7.89<br>8.45 | 3.81<br>3.51 | 4.5<br>3.7 | -<br>1.67 | -<br>3.00 |

| Conditions of sol-gel polycon-densation | Aerogel type | **S$_{BET}$** x10$^{-2}$ [m$^2$/g] | **V**$_{meso}$ [cm$^3$/g] | **r**$_{peak}$ [nm] | **S$_{micro}$** x10$^{-2}$ [m$^2$/g] | **V$_{micro}$** x10$^{2}$ [cm$^3$/g] |
|---|---|---|---|---|---|---|
| R/C= 76;<br>R/F=0.5;<br>R/H$_2$O=0,033 | **RF-β**<br>**C- β** | 7.62<br>8.04 | 3.92<br>3.57 | 5.3<br>4.9 | -<br>1.84 | -<br>4.00 |
| R/C= 97;<br>R/F=0.5;<br>R/H$_2$O=0,033 | **RF-γ**<br>**C- γ** | 6.56<br>6.84 | 3.01<br>2.48 | 5.6<br>3.8 | -<br>1.91 | -<br>5.00 |
| R/C= 102;<br>R/F=0.51;<br>R/H$_2$O=0,033 | **RF-δ**<br>**C-δ** | 6.27<br>6.47 | 2.87<br>2.35 | 5.7<br>3.7 | -<br>1.95 | -<br>5.40 |
| R/C= 108;<br>R/F=0.51;<br>R/H$_2$O=0,033 | **RF-ε**<br>**C- ε** | 6.05<br>6.38 | 2.77<br>2.26 | 5.8<br>3.5 | -<br>2.05 | -<br>5.50 |
| R/C= 75;<br>R/F=0.5;<br>R/H$_2$O=0,141 | **RF-D$_{II}$**<br>**C-D$_{II}$** | 7.35<br>8.39 | 3.34<br>2.78 | 6.9<br>6.1 | 0.88<br>3.07 | 5.00<br>12.00 |
| R/C= 100;<br>R/F=0.5;<br>R/H$_2$O=0,141 | **RF-D$_{III}$**<br>**C-D$_{III}$** | 6.98<br>7.09 | 2.29<br>1.68 | 9.2<br>5.1 | 1.02<br>2.48 | 4.89<br>6.00 |
| R/C= 200;<br>R/F=0.5;<br>R/H$_2$O=0,141 | **RF-D$_{IV}$**<br>**C-D$_{IV}$** | 6.39<br>10.21 | 2.98<br>2.38 | 9.7<br>5.4 | 1.48<br>12.5 | 3.76<br>4.80 |

## 4. CONCLUSIONS

The RF aerogels are mesoporous materials with high surface (600 – 800 m$^2$/g) areas and have few micropores. The mesoporous structure of RF aerogels depends on the R/Na$_2$CO$_3$ and R/H$_2$O ratios used in the sol-gel polycondensation. The RF aerogels have monodisperse porous structures for low mole ratio of resorcinol to basic catalyst or for the high ratio of resorcinol to water. The surface area of RF aerogel can be controlled by the rapport R/Na$_2$CO$_3$. The mesopore volume changes greatly with R/Na$_2$CO$_3$ or R/H$_2$O ratios.

Carbon aerogels have larger surface areas than the corresponding RF aerogels and during pyrolysis of RF aerogels the micropores are formed. Carbon aerogel prepared from RF aerogel having a monodisperse distribution gives a smaller mesopore volume than the RF aerogel.

To control the porous structures of carbon aerogels it is very important to control the structures of RF aerogels.

## ACKNOWLEDGMENT

This research was supported by the Ministry of Education, Research and Youth of Romania, in the frame of MATNANTECH Program, under contract no. C 101(204)/2002.

## REFERENCES

1. S.S. Kistler, *Nature,* 1931, **127**, 741
2. J. Fricke, *Aerogels,* ed. J. Fricke, Springer-Verlag, New York, 1986; pp. 2-19
3. G.M. Pajonk, S.J. Teichner, *Aerogels,* ed. J. Fricke, Springer-Verlag, New York, 1986; pp. 193-199
4. R.W. Pekala, *J. Mater. Sci.,* 1989, **24**, 3221
5. R.W. Pekala, *Mater. Res. Soc. Proc.,* 1990, **171,** 285
6. R.W. Pekala, C.T. Alviso, M. Kong, S.S. Husley, *J. Non-Cryst. Solids,* 1992, **145,** 90
7. R.W. Pekala, D.W. Schaefer, *Macromolecules,* 1993, **26,** 5487
8. R.W. Pekala, *Ultrastructure Processing of Advanced Materials,* D.R. Uhlmanjn, D.R. Ulrich, Eds., John Wiley and Sons, Inc., New York, NY, 1992, 711
9. T.D. Tran, C.T. Alviso, S.S. Hulsey, J.K. Nielsen, R.W. Pekala, *Mat. Res. Soc. Symp. Proc.,* 1996, **431,** 461
10. R.W. Pekala, C.T. Alviso, J.K. Nielsen, T.D. Tran, G.M. Reynolds, M.S. Dresselhaus, *Mat. Res. Soc. Symp. Proc.,* 1995, **393,** 413
11. H. Tamon, H. Ishizaka, *Carbon*, 1998, **36,** 1397
12. H. Tamon, T. Sone, M. Okazaki, *J. Colloid Interface Sci.,* 1997, **188,** 162
13. H. Tamon, H. Ishizaka, T Araki, M. Okazaki, *Carbon*, 1998, **36,** 1257
14. H. Tamon, H. Ishizaka, *J. Colloid Interface Sci.,* 1998, **206,** 577
15. T. Yamamoto, T. Nishimura, T. Suzuki, H.Tamon, *Drying Technology,* 2001, **19 (7),** 1319
16. T. Yamamoto, T. Yoshida, T. Suzuki, S.R. Mukai, H.Tamon, *J. Colloid Interface Sci.,* 2002, **245,** 391
17. D. Dollimore, G.R. Heal, *J. Appl. Chem.,* 1964, **14,** 109
18. B.C. Lippens, J.H. Boer, *J. Catal.,* 1965, **4,** 319