

[Communication]

# Uniform Carbon-covered Alumina Synthesized by Pyrolysis of Sucrose / $\gamma$ -Al<sub>2</sub>O<sub>3</sub>\*

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**Abstract** Carbon-covered alumina (CCA) has been reported to be a promising catalyst support or adsorbent. In the literatures, most of CCAs were prepared by pyrolysis of gaseous hydrocarbon on alumina surface, which was usually not uniformly covered by carbon. In this paper, a simple and novel process has been developed for the preparation of uniform carbon-covered alumina *via* pyrolysis of sucrose highly dispersed on the surface of alumina. In addition, the coverage and number of carbon layers in CCA can be easily controlled by changing the sucrose content in the precursors and the impregnation times.

**Keywords:** Carbon-covered alumina (CCA), Sucrose, Composite material

Carbon-metal oxide composites have been reported as a kind of promising materials in catalysis<sup>[1-8]</sup> and adsorption process<sup>[9-10]</sup> because of their favorable physical and chemical properties. Among them, carbon-covered alumina (CCA) is one of the most intensively studied systems for its beneficial properties of both alumina and carbon<sup>[11-15]</sup>. A synergetic effect may make CCA superior to alumina or carbon in some cases. In the literatures, CCA was usually prepared by pyrolysis of gaseous hydrocarbon, such as acetylene, cyclohexene or ethane. It was reported that the alumina surface was usually not uniformly covered by carbon, probably due to the diffusion limitations of the carbon-yielding hydrocarbon<sup>[11, 16]</sup>. In this communication, a novel and simple method for synthesizing uniform carbon-covered alumina (CCA) *via* pyrolysis of sucrose highly dispersed on the surface of alumina is reported.

## 1 Experimental

Typical synthesis procedure for CCA is as following: at first, sucrose /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> precursors were prepared by impregnating commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with aqueous solutions containing sucrose. The loadings of sucrose in the precursors are shown in Table 1. After drying at 90 °C, the precursors were calcined at 600 °C in flowing N<sub>2</sub> with a rate of 30 cm<sup>3</sup> · min<sup>-1</sup> for 0.5 h. The final products are labeled as CCA01 to CCA08 listed in Table 1. In order to get uniform CCA with higher carbon con-

tent, CCA03-2 was prepared, which precursor was synthesized by impregnating CCA03 with aqueous solutions of sucrose (weight ratio of sucrose to CCA03 was 0.3:1). Similarly CCA03-3 was obtained, which precursor was CCA03-2 covered by sucrose (weight ratio of sucrose to CCA03-2 was 0.3:1). The carbon content of samples was determined by DTA-TG test performed on a Dupont model 1090 apparatus, using  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as reference. Surface areas and pore volume were measured at 77 K on a Micromeritics ASAP 2010 volumetric adsorption system.

**Table 1** Precursor composition, carbon content and texture of CCA samples

Sample	Weight ratio of sucrose to alumina in precursor	Carbon content (w, %)	S <sub>BET</sub> (m <sup>2</sup> · g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> · g <sup>-1</sup> )
Al <sub>2</sub> O <sub>3</sub>	—	0	128	0.48
CCA01	0.1:1	2.0	133	0.46
CCA02	0.2:1	3.9	136	0.45
CCA03	0.3:1	5.7	139	0.43
CCA04	0.4:1	7.4	140	0.40
CCA05	0.5:1	8.8	141	0.39
CCA06	0.6:1	10.0	152	0.38
CCA08	0.8:1	12.7	164	0.35
CCA03-2	—	9.6	141	0.40
CCA03-3	—	12.5	143	0.35

Received: June 11, 2004; Revised: July 15, 2004. Correspondent: Zhu Yue-Xiang (E-mail: zhuyx@pku.edu.cn; Tel: 010-62751703).

\* The Project Supported by NSFC (20173002) and NKBRP (G2000077503)

## 2 Results and discussion

It has been reported that sucrose can be dispersed onto the surface of alumina<sup>[17-18]</sup>. Using the same method, the dispersion capacity of sucrose on alumina employed here was determined to be 0.35 g sucrose/g alumina.

CCA synthesized from sucrose/alumina with different sucrose content show different textures. As can be seen from Fig. 1, CCA03, whose precursor has a sucrose content lower than the dispersion threshold, shows similar adsorption/desorption isotherms as that of alumina; while CCA06, obtained from 0.6 g sucrose/g alumina in which residual crystalline sucrose exists, shows a new capillary step at  $p/p_0$  ca 0.4 ~ 0.7 in its adsorption/desorption isotherms and hence a new peak in its pore size distribution curve. It indicates that in the high-carbon-content CCA samples, a new kind of pores appears. Combined with the results of XRD analysis, it is easy to deduce that this kind of pores should be caused by the carbon resulted from the pyrolysis of the residual crystalline sucrose.

As shown in Fig. 1, CCA03 and alumina have similar pore size distribution, except that the most probable pore diameter decreases from 11.7 nm of alumina to 10.9 nm of CCA03. This change implies that carbon deposits on the surface of alumina uniformly<sup>[11,16]</sup>. In addition, it's worthy to note that the difference between these two diameters is about 0.8 nm, nearly twice of the thickness of a graphite monolayer.

From the pore size distribution of CCA03 and CCA03-2 (shown in Fig. 2), it can be seen that their most probable pore diameters are almost equal, which means that the thickness of the carbon layer in these two samples are similar. Supposing that the entire alumina surface is covered by a layer of carbon in the form

of graphite, the carbon content can be calculated as about  $w = 9.1\%$ . Therefore, the carbon coverage of CCA03-2 with carbon content of  $w = 9.6\%$  is close to one. Assuming that the pores of alumina are cylindrical, the theoretical distribution of uniform CCA with one layer of carbon (named as OLCCA) with coverage of one can be calculated using the method adopted by Vissers *et al.*<sup>[11]</sup>. The theoretical curve of OLCCA is plotted in Fig. 2. It's obvious that the experimentally determined pore size distribution of CCA03-2 is almost identical to that of OLCCA. In addition, with the same assumption, the squared ratio of the most probable pore diameter of  $\text{Al}_2\text{O}_3$  to CCA03-2 is supposed to equal the pore volume ratio of these two samples, and the experimental results coincide with this supposition quite well.

As shown in Fig. 2, the most probable pore diameter of CCA03-3 is only 10.2 nm, which is 1.5 nm lower than that of alumina, and the carbon thickness is almost twice of that in CCA03-2. It indicates that the second layer of carbon appears in CCA03-3. But considering its carbon content, the coverage of the second layer of carbon should be lower than one. Comparison of the experimentally determined pore size distribution and the theoretical one with two layers of carbon (TLCCA) is shown in Fig. 2. These two curves are almost same except that the former curve is a little higher than the latter one. Since the peak area represents the pore volume, this result proves that the coverage of second carbon layer in CCA03-3 is lower than one.

In order to characterize the surface properties of CCA, studies of rhodamine B adsorption were performed on pure alumina, sucrose carbon, CCA03, and the mechanical mixture of alumina and sucrose carbon with the same weight ratio. Sucrose carbon was prepared *via* pyrolysis of sucrose at 600 °C in flowing  $\text{N}_2$  for

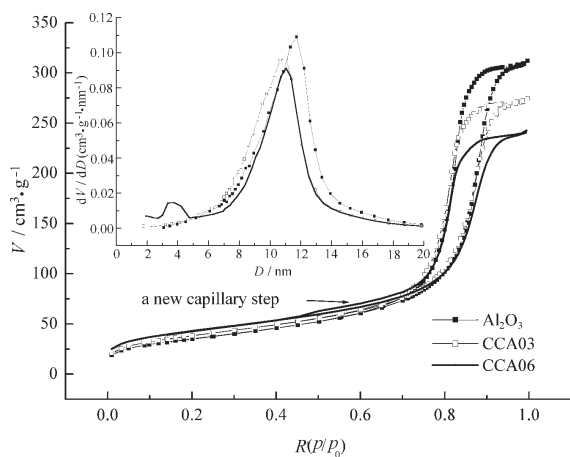


Fig. 1 Nitrogen adsorption-desorption isotherms and pore size distributions (inset) for  $\text{Al}_2\text{O}_3$ , CCA03 and CCA06

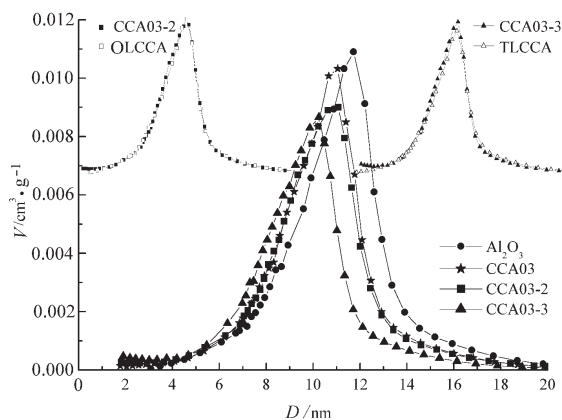


Fig. 2 Comparison of experimentally determined pore size distribution of sample CCA03, CCA03-2, CCA03-3 with theoretical ones of uniform carbon-covered alumina with one and two layers of carbon, named as OLCCA and TLCCA, respectively.

0.5 h as mentioned above. It is found that the adsorption capacity of CCA is much higher than the mechanical mixture of carbon and alumina with the same weight ratio. The unique adsorptive property of CCA should be related to its special texture, and further study is necessary to reveal the fundamental reason.

### 3 Conclusion

In summary, a uniform carbon-covered alumina with different coverage and number of carbon layers can be easily synthesized by controlling the sucrose content in the precursor and the impregnation times. This carbon/alumina composite material shows unique adsorptive properties and is potential for applications as catalysts or catalyst supports.

### References

- 1 Trunschke, A.; Hoang, D. L.; Radnik, J.; Brzezinka, K. W.; Brückner, A.; Lieske, H. *Appl. Catal. A*, **2001**, *208*: 381
- 2 Herrmann, J. M.; Matos, J.; Disdier, J.; Guillard, C.; Laine, J.; Malato, S.; Blanco, J. *Catal. Today*, **1999**, *54*: 255
- 3 Lettmann, C.; Hildenbrand, K.; Kisch, H.; Macyk, W.; Maier, W. F. *Appl. Catal. B*, **2001**, *32*: 215
- 4 Khan, S. U. M.; Al-Shahry, M.; Ingler, W. B. *Science*, **2002**, *297*: 2243
- 5 Tsumura, T.; Kojitani, N.; Izumi, I.; Iwashita, N.; Toyoda, M.; Inagaki, M. *J. Mater. Chem.*, **2002**, *12*: 1391
- 6 Sakthivel, S.; Kisch, H. *Angew. Chem. Int. Ed.*, **2003**, *42*: 4908
- 7 Irie, H.; Watanabe, Y.; Hashimo, K. *Chem. Lett.*, **2003**, *32*: 772
- 8 Tryba, B.; Morawski, A. W.; Inagaki, M. *Appl. Catal. B*, **2003**, *41*: 427
- 9 Leboda, R. *Mater. Chem. Phys.*, **1992**, *31*: 243
- 10 Leboda, R. *Mater. Chem. Phys.*, **1993**, *34*: 123
- 11 Vissers, J. P. R.; Mercx, F. P. M.; Bouwens, S. M. A. M.; deBeer, V. H. J.; Prins, R. *J. Catal.*, **1988**, *114*: 291
- 12 Rao, K. S. R.; Rao, P. K.; Masthan, S. K.; Kaluschnaya, L.; Shur, V. B. *Appl. Catal.*, **1990**, *62*: L19
- 13 Boorman, P. M.; Chong, K.; Kydd, R. A.; Lewis, J. M. *J. Catal.*, **1991**, *128*: 537
- 14 Shekar, S. C.; Murthy, J. K.; Rao, P. K.; Rao, K. S. R. *J. Mol. Catal. A*, **2003**, *191*: 45
- 15 Shekar, S. C.; Murthy, J. K.; Rao, P. K.; Rao, K. S. R.; Kemnitz, E. *Appl. Catal. A*, **2003**, *244*: 39
- 16 Baumgart, J.; Wang, Y.; Ernst, W. R.; Carruthers, J. D. *J. Catal.*, **1990**, *126*: 477
- 17 Xie, Y. C.; Tang, Y. Q. *Adv. Catal.*, **1990**, *37*: 1
- 18 Zhu, Y. X.; Pan, X. M.; Xie, Y. C. *Acta. Phys.-Chim. Sin.*, **1999**, *15*: 830 [朱月香, 潘晓民, 谢有畅. 物理化学学报 (*Wuli Huaxue Xuebao*), **1999**, *15*: 830]

## 热解蔗糖/ $\gamma$ -氧化铝制备碳均匀覆盖的碳/氧化铝复合材料\*

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**摘要** 碳/氧化铝复合材料(CCA)作为催化剂载体或吸附剂具有广泛用途. 在文献报道中, 大部分的碳-氧化铝复合材料是通过热解气相碳氢化合物制得的, 这样在氧化铝表面覆盖的碳通常是不均匀的. 本文提出了一个操作简便, 且重复性高的新方法制备碳均匀覆盖的碳/氧化铝复合材料——热解均匀分散在氧化铝表面的蔗糖. 在这种复合材料中, 碳层厚度可控制为一个石墨单层的厚度, 且碳的覆盖度及层数可以通过改变浸渍的蔗糖量及浸渍次数来进行调控.

**关键词:** 碳/氧化铝(CCA), 蔗糖, 复合材料

**中图分类号:** O643