CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200801323

Carbon-Supported Ruthenium Nanoparticles Stabilized by Methylated Cyclodextrins: A New Family of Heterogeneous Catalysts for the Gas-Phase Hydrogenation of Arenes

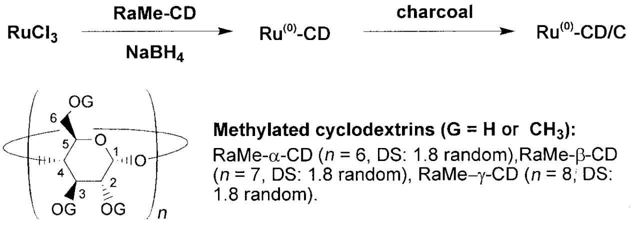
Audrey Denicourt-Nowicki,[a] Alain Roucoux,[a] Frédéric Wyrwalski,[b] Nicolas Kania,[b] Eric Monflier,*[b] and Anne Ponchel[b]

Carbon-supported metal catalysts are widely used in heterogeneous catalysis.[1] Indeed, the carbonaceous materials satisfy most of the desirable requirements for a catalytic support, such as chemical inertness, stability, high surface area, and easy recovery of the metal phase by burning off the spent catalyst. However, the inert nature of the carbonaceous surfaces sometimes makes it difficult to deposit metals, leading to mediocre dispersions of the metallic phase without narrow size distribution.[2]

To overcome these difficulties, carbon-supported nanoparticles prepared by the deposition of stabilized metal colloids onto carbon supports have received considerable attention over the past decade.[3] The stabilization of the colloidal metallic species requires the addition of a protective agent to prevent the aggregation of the colloids into bulk materials. Several articles have offered highly detailed reviews of the specific synthesis techniques for preparing nanoparticles by chemical methods.[4] Concurrently to the stabilization of nanoparticle suspensions, it appears also crucial to consider the affinity of stabilized colloids for the carbon surface to obtain well-defined carbon-supported nanoparticles.

As cyclodextrins (CDs) are known to adsorb spontaneously onto carbonaceous supports[5] and to stabilize metal nanoparticles,[6] we envisaged combining these properties to synthesize new selective heterogeneous catalysts for gas-phase hydrogenation reactions. In fact, we speculated that the anchorage of the metallic nanoparticles on the organic support would be easier in the presence of CD and that these CDs could induce new selectivities through molecular recognition processes. The specific size, shape, and hydrophobic environment of the CD cavity could, for example, enforce the substrates to adopt conformations that are either not or less populated in the proximity of the metal surface or stabilize certain reactive intermediates.

Among the different cyclodextrins described in the literature, the randomly methylated cyclodextrins (RaMe-CDs; Scheme 1) appear to be the best candidates to validate our concept. Indeed, we have recently demonstrated that these methylated CDs can stabilize efficiently Ru^0 nanoparticles in water and that these CD-capped nanoparticles catalyze the hydrogenation of aromatic compounds in water.[6g] Furthermore, we have recently discovered that RaMe-CDs can be easily adsorbed on carbon supports (see Supporting Information).[7]



Scheme 1. Preparation of carbon-supported Ru^0 nanoparticles stabilized by various methylated cyclodextrins.

The carbon-supported ruthenium nanocatalysts were prepared from CD-stabilized aqueous colloidal suspensions, which were obtained by the chemical reduction of ruthenium chloride, followed by their adsorption onto the charcoal support (Scheme 1). The solids are denoted Ru-*x*-RaMe-

---

[a] Dr. A. Denicourt-Nowicki, Prof. Dr. A. Roucoux
Ecole Nationale Supérieure de Chimie de Rennes
Equipe Chimie Organique et Supramoléculaire
UMR CNRS 6226 Sciences Chimiques de Rennes
Avenue du Gal Leclerc, 35700 Rennes (France)

[b] Dr. F. Wyrwalski, N. Kania, Prof. Dr. E. Monflier, Dr. A. Ponchel
Unité de Catalyse et de Chimie du Solide UMR CNRS 8181
Université d'Artois, Faculté des Sciences Jean Perrin
Rue Jean Souvraz SP 18, 62307 Lens Cédex (France)
Fax: (+33) 321-791-755
E-mail: eric.monflier@univ-artois.fr

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200801323.

CD/C, where *x* is the initial molar ratio of RaMe-CD to $RuCl_3$ used to stabilize the colloidal suspension. The adsorbed metal content in the catalysts was determined by elemental analysis and can be averaged to 1.4 ± 0.2 wt% (Table 1).

Table 1. Ruthenium content and BET specific area of the ruthenium carbon-supported catalysts.

Catalyst	Ru [wt%]	BET area [$m^2 g^{-1}$]	Surface loss [%][a]
C (Nuchar)	0	1570	–
Ru/C	1.9	1548	1.4
Ru-3-RaMe-β-CD/C	1.2	830	47
Ru-5-RaMe-β-CD/C	1.5	764	51
Ru-10-RaMe-β-CD/C	1.4	715	54
Ru-3-RaMe-α-CD/C	1.2	724	54
Ru-3-RaMe-γ-CD/C	1.2	924	41
Ru-2-HEA/C	1.8	936	40

[a] Calculated by using the carbon surface (1570 $m^2 g^{-1}$) as a reference.

To investigate the scope limitations of the RaMe-CD as stabilizers, two additional CD-free samples were synthesized. In the first sample, no stabilizer was used and in the second one, the RaMe-CD was replaced by the chloride salt of *N*,*N*-dimethyl,*N*-hexadecyl,*N*-(2-hydroxyethyl)ammonium (HEA), which is a well-known protective agent of ruthenium nanoparticles.[8]

Proof of the adsorption of Ru^0 nanoparticles was first obtained by porosity measurements. Indeed, the textural properties of the support are greatly affected when the nanoparticles were adsorbed onto the charcoal (Figure 1 and Table 1).

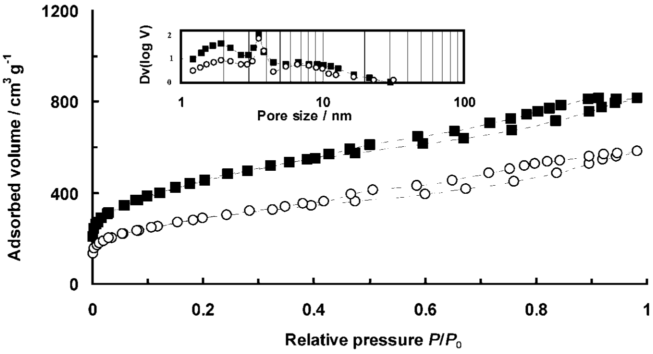


Figure 1. N_2 adsorption isotherms and BJH pore size distributions of the carbon support (■) and Ru-3-RaMe-β-CD/(○).

For instance, the Ru-3-RaMe-β-CD/C sample presents much lower adsorbed amounts of N_2 on the whole isotherm, consistent with much lower specific areas (i.e. 830 vs. 1570 and 1548 $m^2 g^{-1}$ for C and Ru/C, respectively). This phenomenon characterizes unambiguously the adsorption of the CD-stabilized nanoparticles and this adsorption preferentially blocks the entrance of the micropores (≤2 nm). The loss of surface measured with the Ru-2-HEA/C is of the same order of magnitude as that measured with the Ru-3-RaMe-γ-CD/C (41 and 40%, respectively). It is generally agreed that the ease of adsorption of organic compounds on charcoals increases with their molecular mass and decreases with their water solubility.[9] Taking into account that both HEA and RaMe-γ-CD are water soluble, these results indicate that surfactants and RaMe-CDs interact differently with the surface.

The successful adsorption of nanoparticles was further confirmed by thermogravimetric measurements (Figure 2c). Indeed, a rapid weight loss occurs in the 235–400 °C temperature range, due to the thermal decomposition of the CD capping agent.[10] From the weight loss, it can be deduced that about 20% of the introduced amount of RaMe-β-CD is still anchored onto the carbon surface. Thermogravimetric analyses prove also that the supported nanocatalysts are thermally stable up to 235 °C under a nitrogen atmosphere and under a hydrogen atmosphere (see Supporting Information), which is of fundamental importance for catalysis.

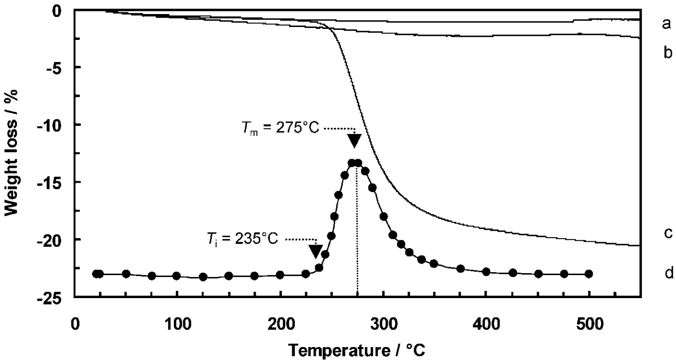


Figure 2. Thermogravimetric profiles under a N_2 atmosphere of a) charcoal; b) Ru/C; c) Ru-3-RaMe-β-CD/C. d) Derivative curve of the TGA profile of Ru-3-RaMe-β-CD/C.

As these results provided evidence of the adsorption of the ruthenium particles protected by RaMe-CDs, their catalytic behavior was investigated in the hydrogenation of *o*-, *m*-, and *p*-xylene in the gas phase at 85 °C. Table 2 reports the steady-state catalytic activities, expressed as turnover frequencies (TOFs), and the selectivities; the only products being the two cyclic products *cis*- and *trans*-dimethylcyclohexane (DMCH). The results presented in Table 2 indicate clearly that carbon-supported Ru^0 nanocatalysts prepared with RaMe-CD-stabilized nanoparticles are more efficient than the classical Ru/C catalyst whatever the substrate. Moreover, the steady-state TOFs reported in the literature for the gas-phase hydrogenation of *o*-xylene at 100 °C with ruthenium systems are 1.5–17 times lower than the best value generated in this work.[11] Notably, RaMe-α-CD and RaMe-γ-CD are less efficient than RaMe-β-CD whatever the substrate. Catalytic activity was also found to be dependent on the CD/Ru ratio. In the case of *o*-xylene, the best result was obtained for a CD/Ru ratio of 3:1 (Table 2, entries 4 and 5). Reproducibility of this optimum has been

Table 2. TOFs[a] and selectivities in xylene hydrogenation at 85 °C on ruthenium catalysts

Entry	Sub.	Catalyst	TOF × 10^3 [s^{-1}]	Sel.$_{cis}$ [%]	Sel.$_{trans}$ [%]
1	*o*-xyl	Ru/C	1.29	98.1	1.9
2	*o*-xyl	Ru-3-RaMe-γ-CD/C	5.73	97.9	2.1
3	*o*-xyl	Ru-3-RaMe-α-CD/C	8.59	98.2	1.8
4	*o*-xyl	Ru-3-RaMe-β-CD/C[b]	14.4	96.1	3.9
5	*o*-xyl	Ru-3-RaMe-β-CD/C[c]	14.6	96.1	3.9
6	*o*-xyl	Ru-5-RaMe-β-CD/C	7.44	97.4	2.6
7	*o*-xyl	Ru-10-RaMe-β-CD/C	9.86	97.2	2.8
8	*o*-xyl	Ru-2-HEA/C	0	–	–
9	*m*-xyl	Ru/C	3.17	92.5	7.5
10	*m*-xyl	Ru-3-RaMe-γ-CD/C	11.3	91.7	8.3
11	*m*-xyl	Ru-3-RaMe-α-CD/C	20.5	91.2	8.8
12	*m*-xyl	Ru-3-RaMe-β-CD/C[c]	30.5	88.6	11.4
13	*p*-xyl	Ru/C	2.78	85.0	15.0
14	*p*-xyl	Ru-3-RaMe-γ-CD/C	10.8	84.7	15.3
15	*p*-xyl	Ru-3-RaMe-α-CD/C	20.0	83.3	16.7
16	*p*-xyl	Ru-3-RaMe-β-CD/C[c]	29.8	78.1	21.9

[a] Turnover frequency defined as number of moles of converted xylene per mole of ruthenium per second. [b] First synthesis batch. [c] Second synthesis batch.

confirmed by using two Ru-3-RaMe-β-CD/C catalysts obtained from two synthesis batches. For a CD/Ru ratio of greater than 3:1 the decrease in activity could be caused by an excess of adsorbed CD on the support, which reduces the accessibility of the substrate to the active metal sites. Astonishingly, no catalytic activity has been measured by using nanoparticles stabilized with HEA (Table 2, entry 8). With regard to the metal content (1.8 %), this result indicates that the metal surface is inaccessible for the substrate when HEA is used as protective agent. This surface effect can be explained by the fact that the long-chain structure of the surfactant is flexible and can form, upon drying, a layer covering the surface that renders the metal particles catalytically inactive, unlike CDs. In fact, this phenomenon could not occur with the nanoparticles protected by CDs due to the rigid structure of the macrocycle.

In terms of the stereoselectivity, the product distribution in the hydrogenation of *o*-xylene shows a preferential formation of the *cis*-1,2-DMCH whatever the ruthenium-based catalyst. This stereoselectivity tendency was in line with that generally observed for the ruthenium-supported catalysts in the hydrogenation of *o*-xylene.[12] Even though *o*-xylene hydrogenation is often considered as a structure-insensitive reaction, Vannice and Rahaman reported that different factors, such as the nature of metal, surface acidity, and metal particle could affect the selectivity.[13] On the basis of the roll-over model proposed by Inoue and co-workers,[14] it is generally considered that the formation of the *trans* product is more energetically demanding and requires a longer stay of the aromatic precursor on the surface, and therefore a stronger adsorption. This could be achieved by strengthening the interactions of the intermediate with the active site. In this context, it should be emphasized that the use of Ru-3-RaMe-β-CD/C results in a twofold increase in *trans*-1,2-DMCH selectivity. This stereoselectivity effect has been further confirmed with the other xylene isomers (Table 2, entries 12 and 16). Indeed, whatever the substrate, the use of RaMe-β-CD as stabilizing agent always improves the catalytic activities and the *trans* to *cis* ratio.

These results cannot only be rationalized by the promoter effect of CDs on the dispersion of the active species. In fact, we assume that the CDs could play an additional role during the catalytic process, through host–guest interactions. Accordingly, the preferential formation of the *trans* product could be linked to host–guest interactions occurring between the gaseous substrate and the CD adsorbed onto the Ru^0 nanoparticles.[15] The ability of solid CDs to interact selectively with gaseous *o*-, *m*-, and *p*-xylene compounds has already been reported for gas-phase chromatography applications through the use of CD-packed columns.[16] Furthermore, it has been observed that the effect of inclusion on the retention followed the same tendency as that observed in reverse-liquid chromatography.[16a] Finally, we have found that *trans*-DMCH selectivities can be connected to the formation constants (K_f) between xylenes and native CDs determined in aqueous media (Figure 3).[17] As clearly shown in the Figure 3, the higher the formation constant is, the higher the selectivity for the *trans* product is.

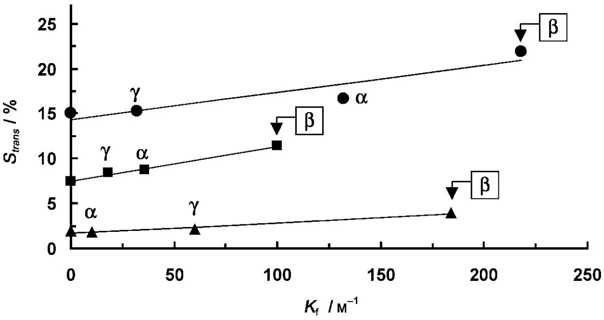


Figure 3. Selectivities for *trans*-DMCH in the hydrogenation of *o*- (▲), *m*- (■), and *p*-xylene (●) versus the formation constants between α-, β-, and γ-CD and *o*-, *m*-, and *p*-xylene.[17]

In summary, carbon-supported ruthenium nanoparticles protected by methylated β-cyclodextrins have been successfully used as heterogeneous catalysts in the gas-phase hydrogenation of benzene derivatives. Originally, the RaMe-β-CDs appeared to be multi-functional molecular receptors capable of stabilizing and dispersing ruthenium particles on the carbon support and of modifying the stereoselectivity through host–guest interactions. In fact, the β-CDs constitute new binding sites (via the hydrophobic cavity) in the proximity of the metal surface, contributing positively to the overall rate of hydrogenation, but more importantly, to the preferential formation of *trans*-DMCH. These results demonstrate that the methylated cyclodextrins can be considered as new tools to develop heterogeneous catalysts for gas-phase reactions.

Experimental Section

General: Randomly methylated β-cyclodextrin (RaMe-β-CD) was purchased from Aldrich Chemicals. Randomly methylated α-cyclodextrin (RaMe-α-CD) and randomly methylated γ-cyclodextrin (RaMe-γ-CD) were prepared by adapting a procedure reported by Y. Kenichi et al.[18] These cyclodextrins were partially methylated. Methylation occurred at positions 2, 3, or 6, and 1.8 OH groups per glucopyranose unit were statistically modified.

Preparation of Ru-*x*-RaMe-CD/C: In aqueous solution, the precursor $RuCl_3$ (90 mL, 0.3×10^{-4} mol) was added to an aqueous solution containing x equivalents of RaMe-α-, RaMe-β- or RaMe-γ-CD (60 mL, $x \times 0.3 \times10^{-4}$ mol). The solution was stirred for 15 min. Sodium borohydride (7.5×10^{-4} mol) in doubly distilled water (50 mL) was added all at once under vigorous stirring at room temperature and the solution was kept under agitation for 2 h at room temperature. Then, charcoal (1 g) was added to the ruthenium(0) colloidal suspension and stirred for an additional two hours. Finally, the catalyst was filtered, washed thoroughly with water (3×40 mL) and dried at 100 °C for 48 h.

Porosity measurements were obtained from nitrogen adsorption/desorption isotherms at $T=-196$ °C with a Nova 2200 apparatus from Quantachrom Corporation. Specific surface areas were calculated from the BET equation using P/P_0 values in the 2.5×10^{-3} and 0.17 range and the pore size distributions were obtained from the desorption branch with the BJH method.

Thermogravimetric measurements were performed by using a SDT 2960 analyzer from TA Instruments, equipped with a flow gas system. The catalysts were treated under a nitrogen atmosphere, and the temperature was allowed to increase at a rate of 2 °C min^{-1} from room temperature to 800 °C.

Typical catalysis procedure: For these reactions, *o*-, *m*-, and *p*-xylene were purchased from Aldrich (99.99 %) and gaseous hydrogen from Air Liquide (99.995 %). Hydrogenation activities were measured at 85 °C, without additional activation steps, in a fixed-bed flow reactor at atmospheric pressure. The hydrogen feed was saturated with vapors (1 kPa) of *o*-, *m*-, or *p*-xylene at 27, 23, and 22 °C, respectively. The total flow rate of the reaction mixture (molar ratio H_2/xylene of 100) was 60 mL min^{-1}. To keep the conversions low (<20 %), small amounts of catalyst were placed in the reactor, that is, 25 and 50 mg for *o*-xylene, and *m*- and *p*-xylene, respectively. The products of the reaction were analyzed in a gas chromatograph (Perkin–Elmer Clarus 500) equipped with a 5 % diphenyl 95 % dimethyl silicon capillary column ($25\text{ m}\times0.25$ mm) and a FID detector. Catalytic activities were evaluated in the steady-state, obtained after about 10 min. Each catalytic run was performed in duplicate and the reported results are the averages of two runs.

Acknowledgements

The authors are grateful to Olivier Gardoll (UCCS-University of Lille, France) for the TG analyses and to Roquette Frère (Lestrem, France) for the generous gift of cyclodextrins.

Keywords: charcoal · cyclodextrins · gas-phase reactions · hydrogenation · metallic nanoparticles

---

[1] a) F. Rodriguez-Reinoso, *Carbon* **1998**, *36*, 159–175; b) H. Marsh, F. Rodriguez-Reinoso, *Activated Carbon*, Elsevier, Amsterdam, **2006**, p. 430.

[2] A. Guerrero-Ruiz, P. Badenes, I. Rodriguez-Ramos, *Appl. Catal. A* **1998**, *173*, 313–321.

[3] a) R. Narayanan, M. A. El-Sayed, *J. Catal.* **2005**, *234*, 348–355; b) C. L. Hui, X. G. Li, I. M. Hsing, *Electrochim. Acta* **2005**, *51*, 711–719; c) S. Ikeda, S. Ishino, T. Harada, N. Okamoto, T. Sakata, H. Mori, S. Kuwabata, T. Torimoto, M. Matsumura, *Angew. Chem.* **2006**, *118*, 7221–7224; *Angew. Chem. Int. Ed.* **2006**, *45*, 7063–7066; d) H. S. Oh, J.G Oh, H. G. Hong, H. Kim, *Electrochim. Acta* **2007**, *52*, 7278–7285; e) C. Y. Lu, M. N. Wey, L. I. Chen, *Appl. Catal. A* **2007**, *325*, 163–174; f) J. M. Nadgeri, M. M. Telkar, C. V. Rode, *Catal. Commun.* **2008**, *9*, 441–446.

[4] a) A. Roucoux, J. Schulz, H. Patin, *Chem. Rev.* **2002**, *102*, 3757–3778; b) B. L. Cushing, V. L. Kolesnichenko, C. J. O'Connor, *Chem. Rev.* **2004**, *104*, 3893–3946; c) D. Astruc, F. Lu, J. R. Aranzaes, *Angew. Chem.* **2005**, *117*, 8062–8083; *Angew. Chem. Int. Ed.* **2005**, *44*, 7852–7872; d) A. Roucoux, A. Nowicki, K. Philippot in *Nanoparticles and Catalysis* (Ed.: D. Astruc), Wiley-VCH, Weinheim, **2007**, pp.349–388.

[5] a) I. Abe, T. Fukuhara, N. Kawasaki, M. Hitomi, Y. Kera, *J. Colloid Interface Sci.* **2000**, *229*, 615–619; b) J. Chen, M. J. Dyer, M. F. Yu, *J. Am. Chem. Soc.* **2001**, *123*, 6201–6202; c) G. Chambers, C. Caroll, G. F. Farell, A. B. Dalton, M. McNamara, M. in het Panhuis, H. J. Byrne, *Nano Lett.* **2003**, *3*, 843–846; d) A. Cassez, A. Ponchel, F. Hapiot, E. Monflier, *Org. Lett.* **2006**, *8*, 4823–4826; e) A. Cassez, N. Kania, F. Hapiot, S. Fourmentin, E. Monflier, A. Ponchel, *Catal. Commun.* **2008**, *9*, 1346–1351.

[6] a) M. Komiyama, H. Hirai, *Bull. Chem. Soc., Jpn* **1983**, *56*, 2833–2834; b) J. Alvarez, J. Liu, E. Román, A. E. Kaifer, *Chem. Commun.* **2000**, 1151–1152; c) L. Strimbu, J. Liu, A. E. Kaifer, *Langmuir* **2003**, *19*, 483–485; d) S. C. Mhadgut, K. Palaniappan, M. Thimmaiah, S. A. Hackney, B. Török, J. Liu, *Chem. Commun.* **2005**, 3207–3209; e) J. Liu, J. Alvarez, W. Ong, E. Román, A. E. Kaifer, *Langmuir* **2001**, *17*, 6762–6764; f) A. Nowicki, Y. Zhang, B. Léger, J. P. Rolland, H. Bricout, E. Monflier, A. Roucoux, *Chem. Commun.* **2006**, 296–298; g) A. Denicourt-Nowicki, A. Ponchel, E. Monflier, A. Roucoux, *Dalton Trans.* **2007**, *48*, 5714–5719.

[7] N. Kania, A. Ponchel, E. Monflier, unpublished results.

[8] a) J. Schulz, S. Levigne, A. Roucoux, H. Patin, *Adv. Synth. Catal.* **2002**, *344*, 266–269; b) A. Nowicki, V. Le Boulaire, A. Roucoux, *Adv. Synth. Catal.* **2007**, *349*, 2326–2330.

[9] M. Manes, D. A. Wohleber, *J. Phys. Chem.* **1971**, *75*, 61–64.

[10] F. T. Trotta, M. Zanetti, G. Camino, *Polym. Degrad. Stab.* **2000**, *69*, 373–379.

[11] P. Reyes, M. E. König, G. Pecchi, I. Concha, M. López Granados, J. L. G. Fierro, *Catal. Lett.* **1997**, *46*, 71–75.

[12] R. Gomez, G. Del Angel, V. Bertin, *React. Kinet. Catal. Lett.* **1991**, *44*, 517–522.

[13] M. V. Rahaman, M. A. Vannice, *J. Catal.* **1991**, *127*, 251–266.

[14] Y. Inoue, J. M. Herrmann, H. Schmidt, R. L. Burwell, J. B. Butt, J. B. Cohen, *J. Catal.* **1978**, *53*, 401–413.

[15] Although studies of host–guest complexes involving solid cyclodextrins and gaseous guests are much less numerous than those in water, several investigations have focused on the complexation of gaseous hydrocarbons, amines, and alcohols by solid cyclodextrins: a) S. Tanada, T. Nakamura, N. Kawasaki, S. Kitayama, Y. Takebe, *J. Colloid Interface Sci.* **1997**, *186*, 180–184; b) M. T. Butterfield, R. A. Agbaria, I. M. Warner, *Anal. Chem.* **1996**, *68*, 1187–1190; c) D. A. Dantz, C. Meschke, H.-J. Buschmann, E. Schollmeyer, *Supramol. Chem.* **1998**, *9*, 79–83; d) A. G. Grechin, H. J. Buschmann, E. Schollmeyer, *Thermochim. Acta* **2006**, *449*, 67–72.

[16] a) T. Kościelski, D. Sybilska, L. Feltl, E. Smolková-Keulemansová, *J. Chromatogr.* **1984**, *286*, 23–30; b) E. Smolková-Keulemansová, L. Feltl, S. Krysl, *J. Incl. Phenom.* **1985**, *3*, 183–196.

[17] N. Szaniszlo, É. Fenyvesi, J. Balla, *J. Inclusion Phenom. Macrocyclic Chem.* **2005**, *53*, 241–248.

[18] Y. Kenichi, M. Atsushi, T. Yukio, S. Mitsukatsu, Y. Yoshiaki, I. Tomoyuki, *JP patent* 8333406 (**1996**).

Received: July 1, 2008