Catalysis Letters 14 (1992) 185–195

# Relation between preparation, porosity and selectivity of CuO-ZnO-MeO$_x$ catalysts in the synthesis of alcohol mixtures

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Received 6 December 1991; accepted 27 March 1992

Some relations between the preparation of modified CuO-ZnO catalysts, their structural properties and their catalytic performance in the hydrogenation of carbon monoxide have been demonstrated. The different activities in the formation of higher alcohols have been attributed to an influence of the porosity on chain growth. The coupling or insertion of $C_1$ intermediates seems to be favoured by an increasing surface coverage with $C_1$ intermediates due to a transport limitation of methanol production. The pore size distribution of the catalysts has been varied by different calcination, thermal ageing, CuO/ZnO ratios, the method of promoting with $Al_2O_3$ and pelleting.

**Keywords:** CuO-ZnO-MeO$_x$ catalysts; characterization by XRD; DTA; adsorption; alcohol synthesis; $C_2$-$C_5$-OH selectivity; influence of porosity

## 1. Introduction

Catalysts on the basis of CuO and ZnO are very active and selective in the hydrogenation of carbon monoxide to methanol [1–3]. There have been many studies about the modification of these catalysts for the synthesis of alcohol mixtures [4]. Some different conceptions about the mechanism of the formation of higher alcohols on copper-zinc oxide catalysts have been published. Coupling of the mechanism for the formation of higher alcohols with that of methanol is generally accepted. The insertion of CO [5], α- and β-addition of $C_1$ or $C_2$ species [6] or the addition of an oxygenated $C_1$ intermediate on the alcohol chain and finally a β-addition of an aldol-condensation type [7] have been discussed. It has been concluded, that the chain-growth rate is much slower than the formation of methanol while the formation of $C_2$ species is the slowest step.

The selectivity for the formation of higher alcohols can be enhanced by promotion with alkaline oxides [8,9]; however, also by the oxides of thorium, chromium and manganese [10,11]. In the network proposed by Nunan et al. [12] for the synthesis of higher oxygenates over Cs-promoted Cu-ZnO catalyst, $C_1$-surface species are also the basis for the chain growth mechanism.

Furthermore, the selectivity for the synthesis of higher alcohols increases with decreasing space velocity [5,13,14]. This fact can be attributed either to the formation of higher alcohols in consecutive reactions of the methanol synthesis [15] or to a common $C_1$ intermediate [16,17] for the formation of methanol and ethanol.

The porosity of the catalyst should also influence the selectivity if the synthesis of alcohols is limited by diffusion of the reaction products out of the pore system. A higher coverage of the copper surface with adsorbed $C_1$ intermediates in the stationary state would favour the chain growing. Some authors have reported on a partial diffusion control in the low pressure synthesis of methanol [18–20]. The diffusion limitation of methanol production should gain in importance at higher reaction temperatures as used for the synthesis of alcohol mixtures. Thus, the change of pore size distribution by addition of oxides of manganese, chromium and thorium to the CuO-ZnO system could be one of the reasons for the enhanced selectivity of higher alcohol formation as described by Hofstadt et al. [10]. A certain pore size range has been claimed for the preparation of catalysts for the synthesis of higher alcohols [21].

## 2. Experimental

### 2.1. CATALYST PREPARATION

The catalyst precursors were prepared by precipitation of the mixed hydroxy-carbonates. An aqueous solution of copper, zinc, manganese or aluminium nitrate (1.0 M, 1.5–2.0 $\ell$) and an aqueous solution of potassium carbonate (1.0 M) were added simultaneously at 353 K to 1 $\ell$ of demineralized water. The rate of addition was 4 $\ell$ $h^{-1}$ and the pH was kept constant at $7.5 \pm 0.2$. The precipitate was aged for 1 h, separated by filtering, washed carefully and dried at 393 K.

Samples A and G were obtained by impregnation of the dried precursors with a solution of aluminium nitrate to promote these catalysts. The precursors were usually calcined at 553 K for 6 h, a part of sample A was calcined at 603 K (cat. B). Then all samples were compressed to form pellets with and bursting pressure of 150 kp $cm^{-2}$, followed by crushing to obtain sieve fractions for the catalytic testing. The composition of the precursors is summarized in table 1.

### 2.2. CATALYST CHARACTERIZATION

The phase composition of the precipitates was determined by powder X-ray diffraction (XRD) using a diffractometer (HZG 4, Präzisionsmechanik Freiberg).

Table 1
Composition, pretreatment and surface areas of the catalysts

| Sample | Composition (wt%) | | | | Precursor phases [b] | BET surface area ($m^2$/g catalyst) | Cu surface area ($m^2$/g catalyst) |
|---|---|---|---|---|---|---|---|
| | CuO | ZnO | MnO | $Al_2O_3$ [a] | | | |
| A | 67 | 30 | 3 | 0.7 i | ZM+AU | 58 | 12.2 |
| B | 67 | 30 | 3 | 0.7 i | ZM+AU | 45 | 11.0 |
| C [c] | 67 | 30 | 3 | 0.7 i | ZM+AU | 22 | 3.3 |
| D | 70 | 30 | – | – | ZM+AU | 62 | 9.0 |
| E | 30 | 70 | – | – | AU | 77 | 15.6 |
| F | 63 | 29 | 3 | 5 c | ZM+HY | 73 | 15.0 |
| G | 65 | 30 | 3 | 2 i | ZM+AU | 44 | 5.5 |

[a] i: impregnated, c: coprecipitated.
[b] ZM: zincian malachite, AU: aurichalcite, HY: hydrotalcite.
[c] C: A tested 1600 h.

Thermal analysis was carried out on samples of dried precipitates (200 mg) which were heated at 5 K $min^{-1}$ to 900 K using a derivatograph of MOM Budapest. The copper surface area of the samples reduced at 573 K was determined by pulse-chromatographic measurement of adsorptive nitrous oxide decomposition. The conditions of the pretreatment of the catalysts and the $N_2O$ decomposition has been proven carefully avoiding overdeterminations by partially reduced ZnO and getting well comparable copper surface areas [22,23].

The pore size distribution of the catalysts was obtained by mercury porosimetry down to 7.5 nm and by measurement of the $N_2$-adsorption isotherms in a range of pore radii from 1.5 to 50 nm. The total surface area was calculated from the $N_2$-adsorption isotherms using the BET equation. Usually, the measurements were performed on calcined precursors. The reductive activation did not change considerably the pore size distribution of the catalysts.

### 2.3. CATALYST TESTING

The catalysts were activated with diluted $H_2/N_2$ mixtures (from 2% $H_2$ up to 75% $H_2$) at stepwise temperature increase from 423 to 513 K. The catalytic hydrogenation of carbon monoxide was performed in three types of integral reactors, i.e. in a microreactor, tube reactor and pilot plant. The microreactor was equipped with mass flow controllers, a pressure controller at the outlet and on line GC. In contrast to the microreactor a top-temperature peak near the gas inlet has been observed in the tube reactor (625 mm, i.d. 6 mm). The top temperature was 20–30 K higher than in the other part of the bed and defined as reaction temperature. The reactor of the pilot plant in Blachownia consists of tubes of 700 cm length. The ring-shaped catalyst bed has a 45 mm i.d. and a 64

Table 2
Activity and selectivity of the catalysts in the hydrogenation of CO

| Sample | MTY (g/kg catalyst h) | | Selectivity (% C) | | | Testing conditions [a] |
|---|---|---|---|---|---|---|
| | $CH_3OH$ | $C_2+OH$ | $CH_3OH$ | $C_2+OH$ | HC | |
| A | 810 | 153 | 70.0 | 21.0 | 8.1 | T |
| B | 1490 | 60 | 90.0 | 6.0 | 3.6 | T |
| A | 415 | 72 | 72.5 | 20.7 | 6.1 | M |
| C | 350 | 7 | 96.6 | 3.2 | 0.2 | M |
| D | 497 | 54 | 80.6 | 14.9 | 4.0 | M |
| E | 468 | 93 | 68.2 | 22.3 | 8.6 | M |
| F | 1610 | 40 | 88 | 3.7 | 7.5 | T |
| G | 962 | 48 | 89 | 6.8 | 3.8 | T |

[a] T: tube reactor, 10 MPa, 593 K, 6000 $h^{-1}$, 10 ml catalyst, 0.8–1.4 mm; M: microreactor, 7 MPa, 583 K, 5000 $h^{-1}$, 0.3 ml catalyst, 0.5–1.0 mm. Synthesis gas: $CO:H_2=1:1$, 4% $CO_2$.

mm o.d. and the size of the pellets is 5 × 5 mm. The reaction temperature is controlled by a Dowtherm cooling system.

The results of testing are only comparable in pairs (table 2) because different pressures and flow rates used in the different reactors influence the activity and the selectivity.

## 3. Results and discussion

The phase composition of the precipitates and the surface area of the catalysts are summarized in table 1.

Comparing the DTA patterns (fig. 1) of samples A and G with those of sample D it is clearly seen that the decomposition of the hydroxycarbonates prepared by impregnation with aluminium nitrate solution proceeds at significantly lower temperatures. Apparently, only the surface of the precipitates is modified by these treatments; no change of the phase composition has been observed.

The different thermal behaviours of the precipitates lead to the formation of differently crystallized copper and zinc oxides by calcination at 553 K. Moreover, small amounts of malachite in the samples D and F as well as aurichalcite in the sample E are observed besides poorly crystallized copper oxide and zinc oxide by XRD. On the other hand the decomposition of the precipitates A and G is complete after calcination at 553 K, as expected from the DTA. Copper oxide and zinc oxide are better crystallized.

In table 2 the activity has been marked by the mass–time yield (MTY) of methanol and higher alcohols. The selectivity for the conversion of CO to alcohols and hydrocarbons is given on the basis of carbon. The remaining difference to 100% is due to traces of esters and ketones.

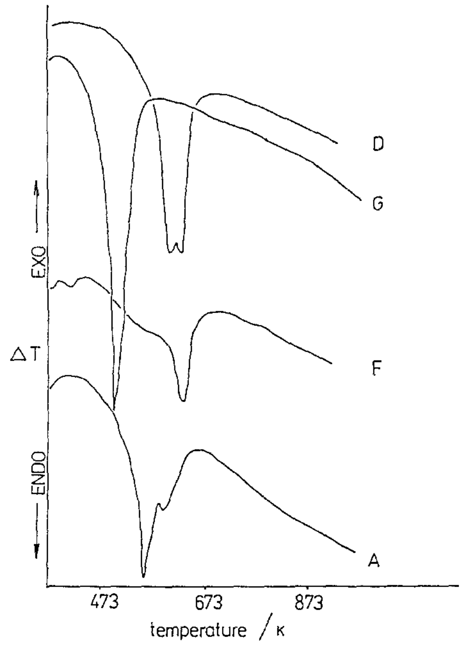

Fig. 1. DTA thermogram of samples A, D, F and G, heating rate 5 K min$^{-1}$.

The product distribution demonstrates a good agreement of the experimental values with the predicted ones calculated by the procedure introduced by Smith and Anderson [8]. Furthermore, the amount of *n*-alcohols follows a Schulz–Flory plot except methanol because its amount is much higher. This corresponds to the literature results about the slow coupling of the first C–C bond.

In accordance with some other authors [24,25,26] we obtained a linear correlation between the copper surface area and the activity of the methanol formation in the kinetic range below 503 K. So we concluded that the formation of methanol takes place on the copper surface. During the ageing of a commercial CuO-ZnO-$Al_2O_3$ catalyst with relatively stable pore structure the formation of higher alcohols decreases nearly proportionally to the decreasing Cu-surface area (fig. 2). Therefore, we have assumed that the formation of ethanol also takes place on the copper crystals or at the interface with ZnO. At the conditions used for the synthesis of higher alcohols we could not generally observe a simple relation between the copper surface area and the activity of alcohol formation because the different porosities of the catalysts influence the alcohol production.

The obtained product distribution seems to be a result of a coupled formation of methanol and ethanol through a common $C_1$ intermediate or by a consecutive reaction of methanol as has been described by Elliot and Pennella [16], Kiennemann et al. [17] or Nunan et al. [12,15]. Further additions of $C_1$ or $C_n$ species lead to the formation of higher alcohols corresponding to the Schulz–Flory

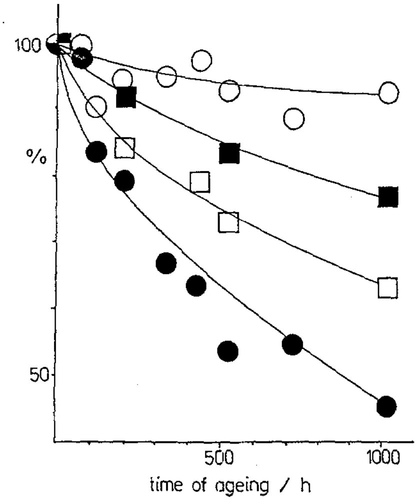

Fig. 2. Thermal ageing of a methanol catalyst at 593 K, changes of copper surface area (●), BET surface area (○); MTY$_{CH_3OH}$ at 503 K/10000 h$^{-1}$ (□), MTY$_{C_2+OH}$ at 583 K/5000 h$^{-1}$ (■).

distribution as well as to the Anderson–Smith distribution. However, the total selectivity of the formation of higher alcohols is determined by ethanol formation as the slowest step. Ethanol formation should depend on the copper surface area and on the coverage of the Cu surface with $C_1$ intermediates. The coverage at the stationary state is higher if the effective competitive production of methanol is limited by the methanol diffusion out of the pores to the surface of the catalyst grains or pellets.

We assume that the larger mesopores and macropores are the channels for transportation of the reaction products. The results of our investigations will be discussed based on this conception.

The catalysts A and B with nearly the same copper surface area show completely different catalytic properties, although they were prepared from the same precipitate. Significant differences in the pore size distribution are obviously caused by the different calcination temperature. More macropores with pore radii above 100 nm (fig. 3a) and less pores below 5 nm (fig. 3b) for sample B have been observed. The activity for methanol formation is higher on sample B, but the activity for the formation of higher alcohols is rather high on catalyst A. This is probably due to a higher coverage with $C_1$ intermediates owing to a transport inhibition of the methanol production on the catalyst A.

A comparison of the data of fresh (A) and aged (C) samples of the catalyst A shows a large decrease in the copper surface area and a shift of the pore size distribution towards larger pore radii (fig. 4) for the aged sample. The large pores are the main reason for the low selectivity for the formation of higher alcohols on the aged catalyst. The formation of higher alcohols is decreased much more than the copper surface area since the part of pores with small

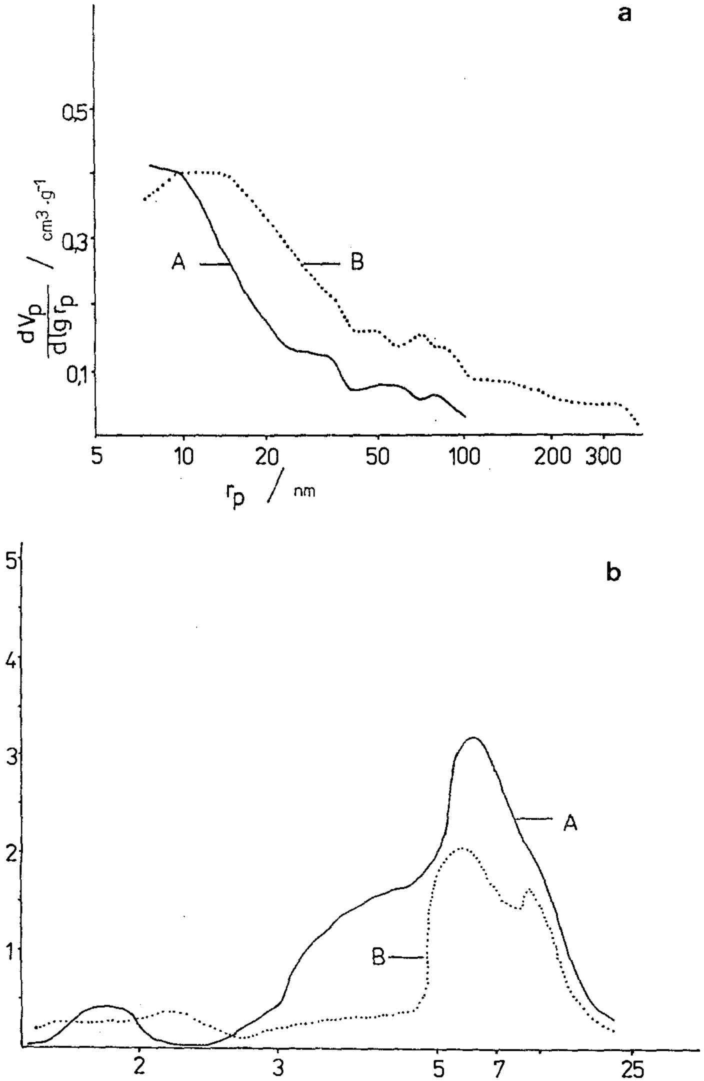

Fig. 3. (a) Pore size distribution of catalysts A and B determined by Hg porosimetry. (b) Pore size distribution of catalysts A and B determined by $N_2$ adsorption.

radius is lower in the aged sample and thus the concentration of $C_1$ intermediates on the copper surface in the pore system is apparently lower. Therefore, the possibility for C–C coupling decreases.

An attempt has been made to vary the porosity of CuO-ZnO catalysts by changing their component ratio (catalysts D and E). Hg-porosimetry has shown similar pore size distribution in the range above 10 nm. But the catalyst E containing more ZnO has more small pores (fig. 5). Furthermore, the copper

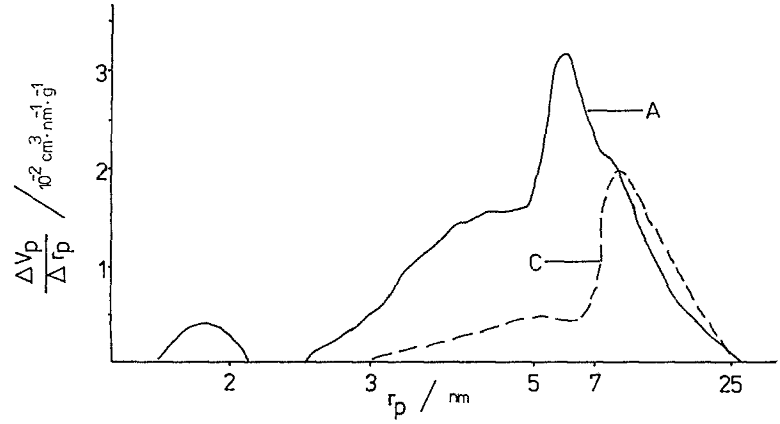

Fig. 4. Change of the pore size distribution by deactivation; (A) fresh catalyst A, (C) 1600 h tested.

surface area of catalyst E is higher than that of catalyst D. However, the stronger inhibition of methanol formation by diffusion favours the chain growth on catalyst E. The formation of higher alcohols and hydrocarbons increases while methanol formation is lower than on catalyst D.

The different properties of the catalysts F and G prepared in various ways can be explained by the different phase composition of the precipitates (see table 1) and their calcination behaviour (fig. 1). After reduction with hydrogen the catalyst F compared with catalyst G yields a higher copper surface area (table 1) and a higher porosity has been observed (fig. 6). Hence, the increase in the formation rate of higher alcohols of the catalyst G compared to F can be

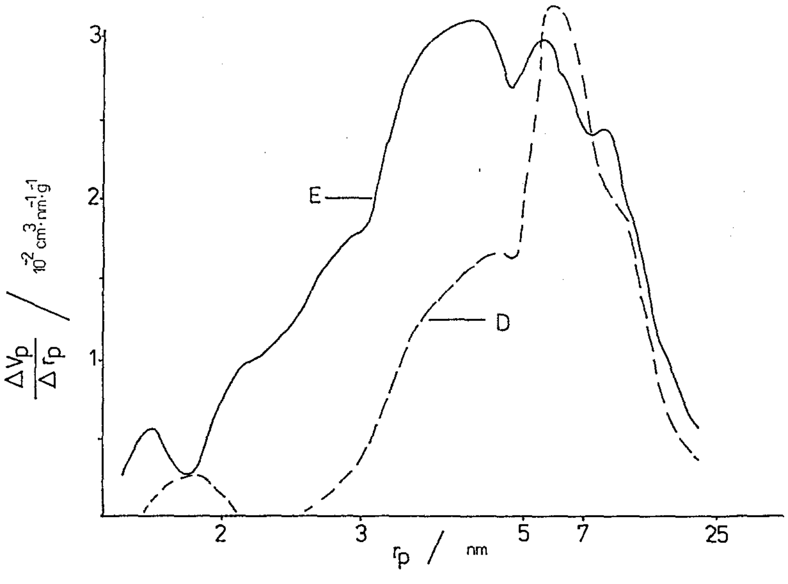

Fig. 5. Pore size distribution of catalysts D and E.

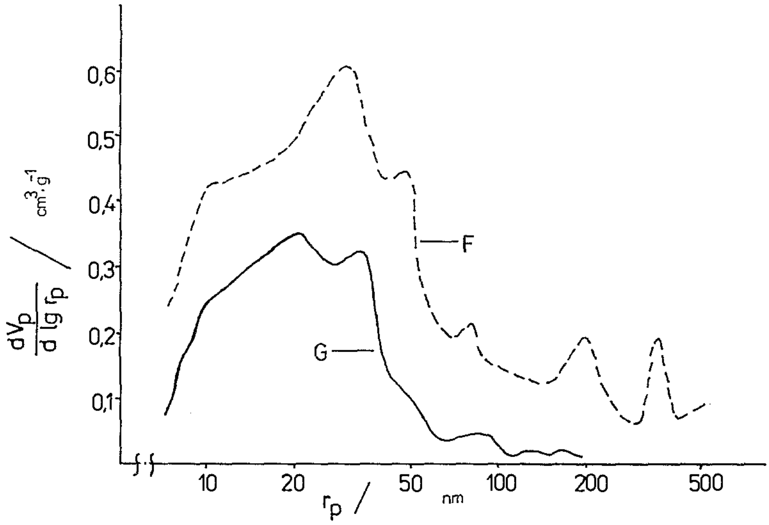

Fig. 6. Pore size distribution of CuO-ZnO-MnO-$Al_2O_3$ catalyst; (F) $Al(OH)_3$ coprecipitated, (G) $Al(NO_3)_3$ impregnated.

explained by the lower amount of transport channels larger than 50 nm. But we cannot exclude that a different distribution of alumina could also play a role. In the case of impregnation more alumina may be located on the surface or at the interface of Cu/ZnO. So Sachtler and Ichikawa [27] proposed that $Al^{3+}$ ions as Lewis centres in the vicinity of an active metal can activate carbon monoxide for insertion to form higher alcohols with an enhanced selectivity.

Finally, the influence of pelleting on the selectivity has been investigated. Cylindrical pellets of 5 × 5 mm with a different density have been prepared from the catalyst H. The different pelletings do not influence the copper surface area (11.4 $m^2/g$ catalyst) and the pore system in the range of small pores. But the

Table 3
Influence of the compression of catalyst H [a] on the activity

| b.p. [b] (kp $cm^{-2}$) | MTY (g $kg^{-1}$ $h^{-1}$) | | GHSV ($h^{-1}$) |
|---|---|---|---|
| | $CH_3OH$ | $C_2$-$C_5OH$ | |
| 160 | 385 | 105 | 3600 |
| 210 | 360 | 115 | 3600 |
| 260 | 340 | 135 | 3600 |
| 160 | 810 | 185 | 8900 |
| 210 | 785 | 210 | 8900 |
| 260 | 720 | 245 | 8900 |

[a] Composition: 63.8% CuO, 31.9% ZnO, 3.7% MnO, 0.6% $Cs_2O$; testing: 12 MPa, 613 K, 46.8% $H_2$, 45.4% CO, 5.1% $CO_2$, 1.9% $CH_4$, 0.8% $N_2$.

[b] Bursting pressure of the pellets.

decrease of the channels between the grains by stronger pelleting changes the selectivity in the hydrogenation of carbon monoxide (table 3). The formation of methanol decreases, while the formation of higher alcohols increases. The diffusion way is longer in the pellets than in the crushed catalyst samples. Therefore, the influence of the porosity is very high.

In summary, it has been demonstrated that the formation of higher alcohols proceeds on the copper or at the interface to zinc oxide using modified Cu-ZnO catalysts. Different preparation and pretreatment conditions clearly influence the pore size distribution of the catalysts. Although there is no direct evidence of the influence of transport limitation of the methanol production upon the formation of higher alcohols it seems very likely that the formation of higher alcohols is considerably determined by the pore structure of the catalysts.

## Acknowledgement

This work was partially supported by the Leuna-Werke AG. Mr. M. Kraft is gratefully acknowledged for the measurements of the pore size distribution. We also acknowledge Dr. B. Peplinski for the XRD investigations.

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