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Creation of Exclusive Artificial Cluster Defects by Selective Metal Removal in the (Zn,Zr) Mixed-metal UiO-66

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ABSTRACT: The differentiation between missing linker defects and missing cluster defects in MOFs is difficult, thereby limiting the ability to correlate materials properties to a specific type of defects. Herein, we present a novel and easy synthesis strategy for the creation of solely 'missing cluster defects' by preparing mixed metal (Zn/Zr)-UiO-66 followed by a gentle acid wash to remove the Zn nodes. The resulting material has the *reo* UiO-66 structure, typical for well-defined missing cluster defects. The missing clusters are thoroughly characterized, including low pressure Ar-sorption, iDPC-STEM at low dose (1.5 pA) and XANES/EXAFS analysis. We show that the missing-cluster UiO-66 has a negligible amount of missing linkers. We show the performance of the missing cluster UiO-66 in CO₂ sorption and heterogeneous catalysis.

Introduction

Since the discrepancy between the real and the expected weight loss in the TGA curves of UiO-661-2 led to the discovery of missing linker defects in MOFs, defect engineering of MOFs has drawn extensive attention. In the last decades, defective MOFs have shown interesting properties not shared by their pristine, non-defective counterparts and several potential applications including gas storage, gas separation, and catalysis have been explored.³⁻⁴ Direct evidence for the presence of missing linker defects was confirmed by high-resolution neutron diffraction and single-crystal X-ray diffraction measurements.⁵⁻⁷ It is noteworthy that another type of defect, namely a missing cluster defect, was observed in MOFs using anomalous X-ray scattering and pair distribution function measurements.8 The missing clusters defects in UiO-66 include the absence of a complete Zr₆ cluster and the surrounding linkers from the secondary building units of the framework, and they result from an unequal distribution of missing linker defects in the modulation synthesis procedure.^{4, 9} The areas in the UiO-66 that have missing cluster defects have the reo topology, in contrast to the normal fcu topology of defect-free UiO-66 (Figure 1). This region can be easily detected by PXRD analysis due to the presence of additional reflections in the diffraction pattern (2theta 3-6°).⁸ Recently, the two kinds of defects have been visualized by high-resolution electron





Figure. 1 UiO-66 with *fcu* topology(left) and UiO-66 with *reo* topology (right).

The modulation synthesis strategy is one of the most common methods to create defects in MOFs.^{3-4, 11} For this method, large amounts of monocarboxylic acids are required, in addition to

the main building blocks/linkers. The monocarboxylic acids (referred to as "modulator") compete with the linkers during synthesis to reduce the crystallization speed, increase the crystallinity, and replace the bidentate linkers that are coordinated to the Zr nodes. This process generates defects in MOFs, and these MOFs are therefore referred to as modulated MOFs, or defective MOFs. A systematic study was carried out by Lillerud's group to evidence a corollary relationship between the amount of modulator and number of defects. In addition, the authors observed that the defect that predominantly results from modulation synthesis is the missing cluster defect.⁹ But also mixed linker approaches are used to create defects. The different thermal stabilities of the different linkers in mixedlinker MOFs were also used to create defects.12 Moreover, hierarchical pore systems (large scale defects) have been developed by numerous methods (e.g., acid selective acid etching,¹² linker labilization,¹³⁻¹⁶ template-assisted routes¹⁷). Zhou's group applied the faster thermolysis of the amino functionalized linker compared to the non-functionalized linker to generate mesopores and highly dispersed ultra-small nanoparticles in these pores during the linker thermolysis process. 12 Bueken et al. used a labile linker, trans-1,4cyclohexane-dicarboxylate, for the UiO-66 synthesis. They observed the exclusive formation of missing linker defects through thermolysis.¹⁸ The formation of a single type of defects allows for the determination of correlations between the type of defect and the observed properties. The other type of defects, the missing cluster defect, is, however, not obtainable via this method. Also, characterization of the type and the distribution of the defects is not evident.

In this work, inspired by the difference in the coordination ability between the linkers and modulators, and the difference in thermal stability between the mixed linkers, we synthesized a set of bimetallic (Zn/Zr)-UiO-66 by varying the ratio of zinc to zirconium. In addition to this, the poor stability of the Zn nodes allows for their selective removal by a soft acid treatment, resulting exclusively in cluster defects. This type of defect is referred to as "artificial cluster defects". This strategy to produce exclusively one type of defect will allow for further insights in defect distribution and its associated properties, previously hindered by the complication of determining structure-property relationships in mixes of two indistinguishable different types of defects. As proof of concept, we explored the effect of the cluster defects on the ring opening reaction of epoxides with a secondary alcohol, as well as the influence on the CO₂ uptake and CO₂/N₂ selectivity.

Results and Discussion

Formation of artificial missing cluster defects by the removal of labile acidic clusters

To synthesize a UiO-66 framework with artificial cluster defects, bimetallic (Zn/Zr)-UiO-66 materials were fabricated with different ratios of Zn/Zr (UiO-66-X, X = mole ratio of Zn to Zr = 0.33; 0.66; 1.0). The synthesis temperature was set at 220 °C, the ideal condition for minimizing the formation of missing linker defects in UiO-66.¹⁹ Due to the different acidic stability of the Zr cluster and Zn cluster, the Zn clusters could be selectively removed by acid treatment, producing the UiO-66 framework with the missing cluster defects.

Powder X-ray diffraction (PXRD) measurements showed that the materials, obtained after a soft wash with 0.1M HCl, maintained the UiO-66 structure, and the diffractions at ca. 4 and 6° (20) are allocated to the 100 and 110 reflections of the reo topology of UiO-66 (Figure 2).8-9 The reo UiO-66 framework refers to the underlying ordered structure with missing cluster defects.8 Shearer et al. studied the missing cluster defects formed by the modulation synthesis method and observed a broad diffraction from 3-7°, attributed to the missing cluster defect.9 Rather than a broad diffraction in this region, two distinct diffractions at 4 and 6° were observed for our samples, evidencing that the reo nano regions are uniformly distributed, having a long-range order, and that the structure was close to the reo topology. These two diffractions were most clearly observed in the UiO-66-0.33 material and are attributed to missing cluster defects. The TEM-EDX elemental mapping results (Fig. S1) show that the Zn-ions were homogeneously distributed in the mixed-metal MOF and confirm the ICP and X-ray absorption spectroscopy (XAS) results that nearly all Znspecies are removed upon mild acid washing.



Figure. 2 PXRD pattern of the *fcu* and *reo* UiO-66 and the UiO-66 samples obtained using different ratios of Zn and Zr. The inset shows an overlap of PXRD patterns from 3 to 6.5° .

XAS measurements at the Zn K-edge (9659 eV) and the Zr Kedge (17998 eV) were performed at CLAESS beamline at the ALBA synchrotron radiation facility (Barcelona). Measurements were performed in transmission and fluorescence mode. Experimental details are given in the supporting information.

For synchrotron-based XAS measurements we have prepared three samples: (i) pristine mixed-metal (Zn,Zr)-UiO-66-0.33 without any washing step (further referred to as S1), (ii) (Zn,Zr)-UiO-66-0.33 after a "soft" washing for 10 mins with distilled water, which already removes most of the Zn (further referred to as S2), and (iii) (Zn,Zr)-UiO-66-0.33 after washing with 0.1M HCl for 10 mins, which nearly completely removes Zn (further referred to as S3).

The absorption jumps at Zn K-edge and Zr K-edge $\Delta\mu_{Zn}$ and $\Delta\mu_{Zr}$ are proportional to the number of Zn and Zr atoms in the sample, respectively, and can thus be used (after accounting for the difference in the absorption cross-sections for Zn and Zr) to check the ratio of Zn and Zr in the MOF samples. The absorption jumps and estimated Zn to Zr ratios are summarized in **Table 1**. ICP-MS data are also given for comparison. One can note that XAS and ICP-MS data are in reasonable agreement, and demonstrate that the Zn concentration is

strongly depleted after "soft" washing, and even more so after washing with HCl.

Sample	Δµzn	Δµzr	Zr to Zn ratio (XAS)	Zr to Zn ratio (ICP- MS)
S1	0.0875	0.299	9.6	6.4
S2	0.0092	2.015	603	859
S3	0.0*	1.923	14600	15500

Table 1 Absorption jump values at Zn K-edge and Zr Kedge, and calculated Zr to Zn ratios. ICP-MS data are also given for comparison. *Note that for S3 sample the concentration of Zn was too low to result in a measurable edge jump at Zn K-edge. In this case, the Zr to Zn ratio was estimated by comparing the Zn fluorescence intensities of S2 and S3 samples, which are proportional to the absorption coefficient.

Thermogravimetric analysis (TGA) is one of the most common methods used to measure defects in MOFs.^{3-4, 11} As shown in Figure 3, the typical TGA curve of UiO-66 displays three main steps. Step 1 consists of the removal of the solvent molecules from the porous framework (desolvation) and is usually completed at T < 150 °C. Step 2 consists of the removal of the two structural water molecules and the compensating ligand of the clusters in the temperature range of ca. 150-350 °C. In a final step 3 the organic parts of the desolvated and dehydroxylated MOF are decomposed to eventually yield ZrO₂. In the case that no defects are present in UiO-66, and all Zrnodes are fully coordinated, the ratio of the molecular weight of six BDC linkers to ZrO2 is 120.8/100. However, it was observed that the TGA curves of different batches of UiO-66 displayed significant differences in the weight loss that occurred at T > 350 °C. More specifically, most of the samples exhibited a smaller weight loss than expected from the ideal chemical formula Zr₆O₆(BDC)₆ of a desolvated and dehydroxylated UiO-66 sample. This discrepancy is attributed to the existence of missing-linker defects in the framework. The amounts of missing linkers can be calculated from this discrepancy. We have analyzed all samples by TGA to determine the amount of the missing linker defects. As shown in Figure 3, the exact ratio of BDC to ZrO₂ for the pristine UiO-66 is 1.13, meaning that we have ca. 0.4 missing linkers per Zr₆ cluster for the pristine UiO-66.

Missing cluster defects are consistently accompanied with missing linkers. For the cluster defected UiO-66-0.33, we calculate from the TGA curve that it has *ca.* 4 BDC linkers per cluster, which matches very well with the *reo* UiO-66 formula, $[Zr_6O_4(OH)_4(BDC)_4]$. The small observed weight loss at 400-500 °C in some TGA curves can be attributed to the incomplete removal of BDC linkers on defects. It also supports the existence of defects, as no weight loss in this area was observed for the pristine UiO-66. An augmented thermal stability (relative to pristine UiO-66) was observed in the materials with artificial cluster defects, despite the fact that the stability of defective MOFs is generally lower than that of the pristine MOF.^{9, 19-20} This is likely a result of the post synthetic acid treatment, which removes the instable sections of the weaker coordinated linkers/clusters.



Figure 3. TGA curves of the UiO-66 samples obtained using different ratios of Zr and Zn.

The surface area increases with the number of defects (UiO-66 (1330 Langmuir m^2g^{-1}), UiO-66-0.1 (1384 Langmuir m^2g^{-1}), and UiO-66-0.33 (1618 Langmuir m^2g^{-1})). The UiO-66-0.33 material exhibits the largest surface area. A similar correlation between surface area and defect quantity was also observed in the work of Shearer et al.⁹ The pore size distributions based on nitrogen sorption (Figure S2) show the appearance of larger pores, which can be attributed to the nano regions formed by missing cluster defects. The pore size distribution of the UiO-66-0.66 and UiO-66-1 material is consistent with previous simulation work and shows the formation of mesopores when large amounts of defects are produced due to the gel polymer as template.²¹

In order to determine the pore distribution in the microporous range, low-pressure argon adsorption measurements were performed. The logarithmic argon isotherms for the UiO-66 and the UiO-66-0.33 are shown in Figure 4. The pristine UiO-66 shows two noticeable condensations of Ar, one around $P/P^{\circ} =$ 10^{-5} and one around P/P° = 10^{-4} . NLDFT analysis of the isotherms results in the pore size distribution in Figure 4, reflecting the two typical pores in UiO-66 of 0.7 and 1.0 nm. This pore size distribution is typical for a "perfect" fcu topology (0.8 and 1.1 nm) (Figure 1). The UiO-66-0.33 shows a different logarithmic isotherm. The first adsorption step around $P/P^{\circ} =$ 10^{-5} is no longer present. The P/P° adsorption around 10^{-4} is still present and a higher-pressure adsorption step is clearly visible around $P/P^{\circ} = 10^{-2}$. This corresponds to the pore size distribution in Figure 4, showing pores at 1.0 nm and at 1.7 nm (Figure 1). The corresponds perfectly to the UiO-66 with missing clusters in the reo topology (1.1 and 1.8 nm). These pore size distributions are strong evidence for the creation of reo topology cluster defects and corroborate the XRD and TGA findings.



Figure. 4 Argon adsorption isotherms of UiO-66 and UiO-66-0.33 and the insert shows argon adsorption isotherms of UiO-66 and UiO-66-0.33 in logarithmic scale. (top) and pore size distribution of UiO-66 and UiO-66-0.33 according to non-local density functional theory (bottom).

Electron microscopy characterization of such beam sensitive samples is extremely challenging and the framework structure will quickly degrade even when low electron doses are applied. Therefore, most electron microscopy investigations of MOFs have been performed in transmission electron microscopy (TEM) mode, using a parallel beam. However, because of the contrast transfer function, post-processing is required to correctly interpret the image contrast.¹⁰ Integrated differential phase contrast (iDPC) in scanning TEM (focused beam) is a relative novel approach which enables to obtain images using very low electron doses (below 300 e/A² in this case). iDPC-STEM images can be more directly interpreted and the technique has been used successfully in the characterization of MOFs recently.¹⁰ To correctly visualize the missing clusters in the UiO-66-0.33 sample, the structure must be oriented along the 100 zone axis. In Figure 5, we show such an image, where at the top-left area of the oriented particle the absence of the cluster is confirmed.



Figure. 5 Theoretical models of fcu UiO-66 and reo UiO-66 along the 100 zone axis showing the missing cluster (top). iDPC-STEM image of an UiO-66-0.33 particle oriented along the 100 zone axis. Areas with missing cluster structure (*reo*) are indicated by dotted yellow rectangles the non-defective *fcu* areas are indicated by green dotted rectangles. The inset is showing a magnified image of a unit cell with (right) and without (left) a defect.

In order to investigate in more detail whether the original (Zn,Zr)-UiO-66 consist of truly mixed metal clusters or rather of an amorphous ZnO contribution, extensive XAS data analysis was performed, including analysis of X-ray absorption neare edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analysis.

The Zr K-edge and Zn K-edge XANES spectra after normalization are shown in Figure 6 (a) and (b), respectively. Spectra for reference oxides (ZnO and ZrO₂) are also shown for comparison. XANES spectra suggest that both Zn and Zr are in a completely oxidized state, with oxidation states 2+ and 4+, respectively. Zr K-edge XANES data are in good agreement with those published for (Ce, Zr)- UiO-66 MOFs²² and are very similar to the spectrum of ZrO₂. One can also note that for the three MOF samples investigated (S1, S2, S3), the Zr K-edge XANES are very similar, with the XANES spectra for samples S2 and S3 being nearly indistinguishable, implying that the soft acid wash removal of the Zn species has no significant impact on Zr species. At the same time, XANES data collected at Zn K-edge suggest a strongly disordered structure. The washing treatment not only removes Zn species from the sample, but also affects their local structure. Moreover, the main XANES feature at ca. 9665 eV is shifting to higher energies, when going from sample S1 to S2, to S3. In the latter case, the position of this main Zn K-edge XANES feature is close to that in ZnO. We tentatively attribute this shift to the changes in Zn-O interatomic distances,²³ which appear to be longer in the pristine sample than in ZnO, but, upon washing, are reduced.

Fourier transformed (FT) EXAFS spectra for the MOF samples and reference oxides are shown in Figure 6 and Figure S6. The EXAFS data are in a good agreement with XANES data. At the Zr K-edge (Fig. S6) we observe that EXAFS spectra for all MOF samples are similar. Inspection of Fourier-transformed Zr K-edge EXAFS data (Fig. 6) confirms this conclusion. FT-EXAFS spectra are similar to those reported for Zr K-edge in (Ce, Zr)-UiO-66,²² and are dominated by two peaks, one at the ca. 1.5 Å, the other at ca. 3.2 Å. The first peak is assigned to the contribution of Zr-O bonds, and its position and intensity are similar to the ones in ZrO₂. The second peak is attributed to Zr-M bonds (here M is Zn or Zr). This peak is shifted to larger interatomic distances than the Zr-Zr peak in ZrO2. Moreover, we observe a systematic decrease in the intensity of this peak when moving from sample S1 to S2, to S3. The lack of significant changes in the position of this peak for different samples is a strong indication that in all the cases this peak corresponds to the same type of bond (i.e., Zr-Zr), and the contribution of heterometallic Zr-Zn bonds is not significant.

At the Zn K-edge, we observe that the mismatch between the EXAFS frequencies for the MOF samples and ZnO reference is more pronounced. In sample S3 the first EXAFS features resemble those in ZnO, but with suppressed amplitude, suggesting that the remaining Zn species may be present in this MOF sample in the form of disordered oxide clusters. The Zn K-edge Fourier transformed EXAFS is dominated by a single peak at ca. 1.5-2 Å, which corresponds to Zn-O bonds. In the pristine sample S1, this peak is noticeably shifted to larger interatomic distances in comparison to that in ZnO reference. Upon washing treatment, however, this peak shifts to shorter interatomic distances, and in sample S3 it is at a position roughly corresponding to the Zn-O peak position in ZnO. The shift of Zn-O peak is paralleled by its broadening, which reveals a significant increase in the structural disorder around the Zn species. Crucially, the contribution of distant coordination shells is relatively weak in Zn K-edge EXAFS, and only a small broad peak is present at R values ca. 3-4 Å. For sample S3, only the first peak can be identified reliably: the other peaks in FT-EXAFS for this sample are artifacts due to very low Zn loading and, consequently, poor EXAFS data quality.

For quantitative EXAFS analysis, we performed a non-linear least square fitting of the EXAFS data. At the Zr K-edge we fitted the contributions of the first two coordination shells, for the Zn K-edge only the first coordination shell could be analyzed. The results and details of this fitting are described in the supporting information (Figure S7, S8 Table S1, S2). In summary, the Zr-Zr bond length $(3.534 \pm 0.003 \text{ Å})$ was in all samples significantly larger than Zr-Zr distance in ZrO₂, and is in an excellent agreement with the Zr-Zr distance reported for (Ce, Zr) UiO-66 MOF (3.529 ± 0.003) .²². The inclusion of Zr-Zn path did not improve the fit quality. Thus, Zr K-edge EXAFS data analysis does not suggest the presence of mixed Zr-Zn clusters. One should note, however, that due to the large Zr to Zn ratio in our samples, the contribution of Zr-Zn bonds is expected to be low in any case The Zn-species (minority species) should be more sensitive to the presence of Zn-Zr clusters. We interpret the lack of the distant coordination shell contributions in the Zn K-edge EXAFS as an indication of the lack of mixed Zr-Zn clusters in our samples. .

Based upon these observations, we can argue that the Zn nodes have disordered structure and are selectively and nearly completely removed by washing to create cluster defects.



Figure. 6 Zr K-edge (a) and Zn K-edge (b) XANES spectra for UiO-66 MOF samples S1, S2 and S3, and for reference oxides. Fourier-transformed (FT) EXAFS spectra at Zr K-edge (c) and Zn K-edge (d) E for UiO-66 MOF samples S1, S2 and S3, and for reference oxides.

The correlation between the catalytic performance and the number of defects

To explore the correlation between the catalytic performance and the number of cluster defects, we investigate a catalytic ring opening reaction. The relation between the number of open Zrsites caused by defects and the catalytic activity in this reaction was previously addressed by Farha's group.24 The number of defects was quantified via titration.²⁵ The defects, compensated with hydroxide/water, are Brønsted sites, and are the active sites in the ring opening reactions. In this work, the ring-opening of styrene oxide with isopropanol was examined under reaction conditions similar to those used by Farha. In accordance with the two possible sites of nucleophilic attack of the monohydric alcohols onto styrene oxide, two products are possible: the primary alcohol (A, β-alkoxy alcohols), and the secondary alcohol (B). Alcohols have a poor nucleophilicity and Brønsted acid catalysts improve the alcoholysis of epoxides to obtain the main product, β -alkoxyalcohols. The ionized protons attack the oxygen atom of styrene epoxide to form the electrophilic benzyl carbocation and thus the nucleophilic alcohol would mainly attack the benzyl carbocation resulted in the primary β alkoxyalcohols.26

In Table 2, the conversion of the four examined materials is presented together with that of a reference material, MOF-808. We also ran a blank reaction, showing no conversion at all. MOF-808 was first tested, yielding similar results to previously recorded observations.²⁴ The pristine UiO-66 exhibited a low conversion (17%), which was expected due to the nearly defect-free structure. In contrast, the UiO-66-0.33 showed 90% conversion of styrene oxide, comparable with the catalytic activity observed for the NU-1000 framework. The UiO-66-

0.33 possesses ca. 4 missing linker defects per cluster. In other words, it can be seen as an 8 - fold coordinated *reo* UiO-66 structure, similar to the 8-fold coordination of Zr in NU-1000.



Table 2.	Conversion	of styrene	oxide	after	24 h	with	various
MOFs							

The correlation between the CO₂ uptake and the number of defects

To study the effect of the missing cluster defects on the CO_2 storage and separation performance, the CO_2 uptake of all the samples was measured and are reported in Table 3. It was observed that the CO_2 uptake increased (UiO-66-0.33 > UiO-66-0.1 > UiO-66) with increasing number of defects.

Sample	CO ₂ (mmol/g) 273K	uptake 298K	Q _{st} (KJ/mol)	CO ₂ /N ₂ Select ^a
UiO-66	3.02	2.11	22.6	24
UiO-66-0.1	3.28	2.01	23.3	27
UiO-66-0.33	3.58	2.17	25.1	45
UiO-66-0.66	2.68	1.59	21.1	30
UiO-66-1	2.43	1.43	22.2	36

Table 3. CO_2 adsorption uptakes, CO_2 adsorption of isosteric heat (Q_{st}), and CO_2/N_2 selectivities of UiO-66 samples obtained using different ratios of Zn and Zr.

^aThe selectivity was calculated by the Henry model.

The CO₂ uptake capacity at low temperatures is predominately influenced by the interaction of the CO2-sorbent with the framework.²⁷ As seen in Table 2, the UiO-66-0.33 has the highest CO₂ capacity; 16% higher than the pristine UiO-66 (3.58 mmol/g vs 3.02 mmol/g at 273K). In addition, UiO-66-0.33 has the highest isosteric heat of CO₂ adsorption. This is due to a combination of an increased number of unsaturated sites and an increased surface area, as a result of the defects and is consistent with previous works.5, 28 As shown in the study of Liang et al., the vacancies compensated by either -OH or Cl have stronger binding sites than the perfect, non-defective samples.²⁸ It is important to note that the CO₂/N₂ selectivity of UiO-66-0.33 was roughly twice as high as that of the pristine UiO-66 (24 vs. 45). The high CO₂/N₂ selectivity of the UiO-66-0.33 material suggests quadrupolar interactions between CO₂ and the defect sites.29

Despite the greater number of defect sites in UiO-66-1 than in UiO-66-0.66, the CO_2 uptake of the latter is higher than that of UiO-66-1, and both materials show a lower uptake than UiO-66-0.33. This is likely a result of the presence of mesopores, originating from the large-scale defects, which do not favor CO_2 adsorption at low pressures.

Conclusion

Defects influence various properties of materials, and defect engineering is an efficient toolbox for task-specific applications. The inability to distinguish between types of defect in MOFs complicates the study of the relationships between the structure and the properties. This work expounds upon a method to use the different acid resistance of clusters in MOFs to create exclusively one type of defect: the missing clusters defect. UiO-66-0.33 was created by a soft acid wash of a mixed-metal (Zn,Zr)-UiO-66, that removed the Zn-sites to form a Zr-UiO-66 with artificial cluster defects with a reo topology. The structure and composition of this material was verified by XRD, TGA, STEM-iDPC, XANES, EXAFS and was confirmed to contain almost no missing linker defects, nor residual Zn. The effects of this type of defect in catalysis and adsorption could then be explored. The catalytic activity of the ring opening reaction and the CO₂ capacity both show positive correlations with the number of defects, and defect sites exhibit increased CO₂/N₂ selectivity. This method can be expanded to other types of MOFs.

ASSOCIATED CONTENT

Supporting Information.

Detailed procedures for synthesis and characterization, SEM-EDX, TGA analysis, Nitrogen and CO₂ sorption isotherms, EXAFS and XANES characterization (PDF) This material is available free of charge via the Internet at http://pubs.acs.org.

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