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Cite this: DOI: 10.1039/c0xx00000x

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COMMUNICATION

Preparation and Oxygen Storage of Cadmium-modified Zeolites with Superior Electron Transfer Capacities

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Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X
DOI: 10.1039/b000000x

A cadmium-modified zeolite with superior electron transfer capacities has been prepared by the incorporation of cadmium vapor into the channels of a dehydrodrated HZSM-5 (protonated zeolite ZSM-5). This Cd-containing zeolite material possesses superior oxygen storage property. Meanwhile, univalent Cd^+ species can be observed for this zeolite under the ultraviolet irradiation.

Zeolites have been widely used in many fields, [1] such as catalysis, ion exchange, and separations. They are crystalline aluminosilicates, with lots of channels and cages of molecular dimensions dispersed in their framework. Various cations or clusters (including Zn_2^{2+}, Na_4^{3+}, Ag_3^{2+}, etc.)[2-5] can be implanted into the channels of the zeolite, generating electron-rich composites. Among them, a particular type is zinc-modified zeolite with accessible electrons delocalized on the zeolite framework in the vicinity of zinc cations.[6-8] For the high reactivity of the delocalized electrons in combination with regular porous structures of zeolite, these electron-rich materials possess unusual properties. For example, the electron-rich zinc-modified zeolite Y can act as an efficient activator to decompose thermodynamically stable CO_2 molecules into carbon and oxygen under relatively mild condition.[7]

$$Cd + HZSM\text{-}5 \longrightarrow CdZSM\text{-}5 + 1/2H_2 \qquad (1)$$

Cadmium-modified zeolite is one storage material for gases, which offers the possibility of selective separation of gases from mixed streams.[9-11] A variety of techniques,[10-14] such as ion exchange from aqueous solutions, impregnation, or chemical vapor deposition at high temperature, have been proved to be successful for the preparation of cadmium-modified zeolite. However, electron-rich cadmium-modified zeolite material is not obtained by these techniques. In this communication, we report on the formation of electron-rich cadmium-modified zeolite by exposing the dehydrated HZSM-5 to cadmium vapor under vacuum. In comparison with the previously-reported cadmium-modified zeolite, our preparation route is highly advantageous because the cadmium-modified zeolite contains a large number of delocalized electrons, and it exhibits superior oxygen storage capacity and can be used as $^{\bullet}O_2^-$ radicals reservoir for the reactions that radicals and *in-situly* generated highly active O_2 are essential. More importantly, the electron-rich cadmium-modified zeolite obtained through this vacuum approach can produce univalent cadmium (Cd^+) species in the zeolite. As is known, Cd^+ is a strong reducing ion, which usually formed by the reaction of hydrated electrons with Cd^{2+} cations.[15, 16] Most of the produced Cd^+ species only exist the dissolution of cadmium metal in molten cadmium dihalides.[17] These molten preparation techniques usually consumes a lot of energy resources, sometimes involving tedious treatments. To date, the preparation of these Cd^+ species is still full of challenge. In our work, it is found that upon the irradiation of ultraviolet (UV) light, the electrons have transferred from the zeolite framework to the nearby Cd^{2+} cations, the latter becoming Cd^+ species. This provides a new novel method to preparation of Cd^+ species.

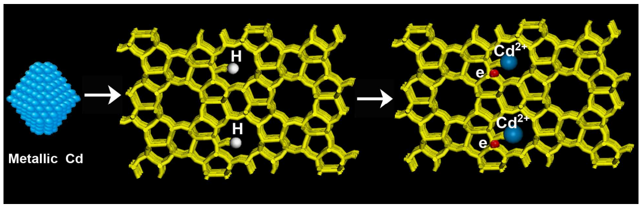

Fig. 1 Schematic representation of the formation of electron-rich cadmium-modified zeolite ZSM-5 material through the vapor-solid reaction (yellow: the zeolite framework; Cd: blue; H: white; electrons: red).

The electron-rich cadmium-modified zeolite was prepared through a solid-vapor reaction route under vacuum (Fig. 1), following the procedure described previously.[7] Typically, metallic cadmium was placed in an end-closed glass tube, next to dehydrated zeolite ZSM-5 (HZSM-5, Si/Al molar ratio = 14.8). After evacuated at 400 °C for two hours to remove the water and other species adsorbed in the microspores of HZSM-5, the glass tube was sealed and further heated at 450 °C for approximately 40 hours to allow vaporized metallic Cd to react with the protons of the Brønsted acidic sites (OH groups bridging Al and Si atoms of the framework) in HZSM-5 (Fig. S1, ESI†). In order to make sure that no neutral cadmium species were physically adsobed in the zeolite, the sample after the reaction was evacuated at about 420 ºC for six hours. During the solid-vapor reaction, the protons of the Brønsted acidic sites in the zeolite are reduced by cadmium atoms to form H_2 molecules [eqn (1)], whereas the cadmium atoms undergo two different oxidations: One is that each cadmium atom reduces two closely-positioned protons to form a Cd^{2+} cation; the other is that each cadmium atom reduces one isolated proton to form a Cd^{2+} cation with an extra electron delocalized on the zeolite framework. Delocalization of electrons on the zeolite framework has been reported previously, [18, 19] and the delocalized electrons do not give rise to electron paramagnetic resonance (EPR) signals.[6] This cadmium-modified zeolite containing delocalized electrons is abbreviated as CdZSM-5. According to inductively coupled plasma (ICP) elemental analysis, the composition of CdZSM-5 is $Cd_{0.69}AlSi_{14.8}O_{31.6}$. For comparison, conventional Cd^{2+}-exchanged ZSM-5 material (designated Cd^{2+}-ZSM-5) was also prepared through ion exchange of $Cd(NO_3)_2 \cdot 4H_2O$ with HZSM-5 in an aqueous solution. The adsorbed water molecules within Cd^{2+}-ZSM-5 were removed by evacuation at about 450 °C as well. The composition of the Cd^{2+}-ZSM-5 is $Cd_{0.49}AlSi_{14.8}O_{31.6}$ on the basis of the ICP analysis. ICP elemental analyses indicate that the molar ratios of Cd/Al in CdZSM-5 and ion-exchange Cd^{2+}-ZSM-5 are approximately 0.69 and 0.49, respectively. Obviously, the cadmium content of the CdZSM-5 sample is considerably higher than that of the Cd^{2+}-ZSM-5 sample. This observation is reasonable because there are extra (delocalized) electrons in CdZSM-5 whereas Cd^{2+}-ZSM-5 has no such extra electrons. These extra electrons, besides the negative charges of the zeolite framework, require more Cd^{+} cations to balance their charges. Because the molar ratio of Cd/Al in the CdZSM-5 material is 0.69, it is calculated that about 55% of the incorporated Cd atoms reduce one proton per Cd atom and the rest (45%) of the Cd atoms reduce two protons per Cd atoms (Supporting Information, ESI†). Therefore, the cadmium species remaining in the CdZSM-5 material after the solid-vapor reaction should be isolated Cd^{2+} cations, some of which are accompanied by delocalized electrons in their vicinity. Meanwhile, no obvious difference is observed in the powder X-ray diffraction patterns of CdZSM-5, Cd^{2+}-ZSM-5 and HZSM-5, indicating that the solid-vapor reaction under vacuum and ion-exchange processes for the preparation of CdZSM-5 and Cd^{2+}-ZSM-5 have negligible influence on the framework structure of HZSM-5 (Fig. S2, ESI†).

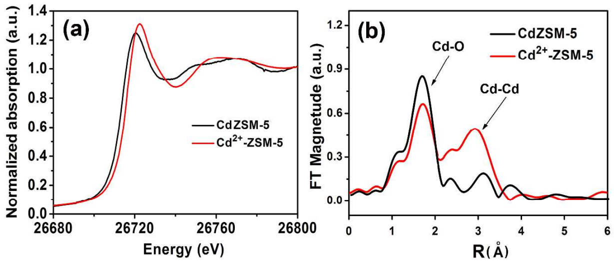

Fig. 2 (a) XANES spectra of the CdZSM-5 and Cd^{2+}-ZSM-5 samples, and (b) Fourier-transformed EXAFS spectra for Cd K-edge of the CdZSM-5 and Cd^{2+}-ZSM-5 samples.

Previous studies have demonstrated that the position of the absorption edge in XANES spectra is correlated with the valence state of the absorbing atom.[20] With increase of oxidation state, the absorption edges usually shift towards higher energies.[21] Fig. 2a shows the XANES spectra of the CdZSM-5 and Cd^{2+}-ZSM-5 samples. The absorption edge of the CdZSM-5 material for Cd K-edge is at approximately 26713 eV, an energy value lower than that of ion-exchanged Cd^{2+}-ZSM-5 (26714.5 eV).[22] As is known, the oxidation state of cadmium in Cd^{2+}-exchanged zeolite is +2.

The absorption edge of the cadmium-modified zeolite ZSM-5 indicates that one intermediate oxidation state of cadmium cations exists in the sample. It is presumable that the unusual nominal oxidation state for cadmium arises from the possible existence of Cd^{2+} cations with delocalized electrons in the vicinity. The Fourier-transformed EXAFS spectra of the CdZSM-5 and Cd^{2+}-ZSM-5 samples measured at Cd K-edge are shown in Fig. 2b and the main corresponding structural parameters are listed in Table S1. Main features of Cd-O and Cd-Cd connections are observed for the ion-exchanged Cd^{2+}-ZSM-5 sample, but only the Cd-O connection is observed for the CdZSM-5 sample, suggesting better dispersion of cadmium cations in CdZSM-5 sample. Given the fact that there are no oxygen molecules in the reaction system, the oxygen shell backscatterers can only be from the zeolite framework. During the calculation at Cd K-edge, [23] the Cd cations in the sample are coordinated by about 3.9 oxygen atoms on average, and the oxygen shell backscatterers at 2.25 Å (Table S1, ESI†), a value close to the Cd-O bond distance observed for compounds with divalent cadmium cations tetra-coordinated by oxygen.[24] This observation indicates that the Cd^{2+} cations may partly coordinated with four and partly with three oxygens, with the average coordination number (*N*) being about 3.9. From the XANES and the EXAFS spectra, we conclude that in the CdZSM-5 material, the cadmium cations are divalent, some of which each possess a nearby electron over the zeolite framework, and this nearby electron makes the Cd K-edge X-ray absorption shift toward lower energies.

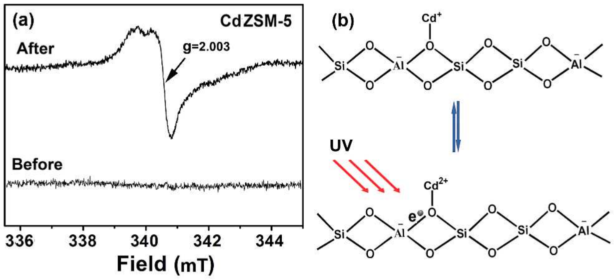

Fig. 3 (a) *In situ* EPR spectra for the CdZSM-5 sample before and after the irradiation of UV light under room temperature, and (b) the schematic representation for the Cd^{+} species generation from the electron-rich zeolite ZSM-5 framework under the UV irradiation.

To further confirm the existence of extra electrons, the as-prepared CdZSM-5 material was subjected to the irradiation of ultraviolet (UV) light from a 150 W high-pressure Hg lamp for one hour. The electron paramagnetic resonance (EPR) spectra were recorded before and after the UV irradiation (Fig. 3a). The EPR spectrum measured in vacuum before the UV irradiation shows no obvious EPR signals. Previous studies indicated that it is possible for extra electrons to be delocalized on the zeolite framework, [6, 7] and these delocalized electrons do not show EPR signals. The silence in the EPR spectrum indicates that no obvious unpaired electrons are present for the as-prepared CdZSM-5 material. However, a distinct EPR signal with a g value of 2.003 is observed after the UV irradiation for the CdZSM-5 sample. Because both the zeolite framework and Cd^{2+}

cations are EPR-silent, the only possibility for the appearance of the EPR signal with a g value of 2.003 is the formation of isolated Cd^+ cations in the zeolite.[25] Under the UV radiation, delocalized electrons are promoted from the zeolite framework to the nearby Cd^{2+} cations, the latter becoming Cd^+ species (Fig. 3b). For comparison, the ion-exchanged Cd^{2+}-ZSM-5 material was irradiated similarly under the UV irradiation, but no EPR signal appears at all in this case for the Cd^{2+}-ZSM-5 sample (Fig. S3, ESI†), which has no extra electrons on the zeolite framework.

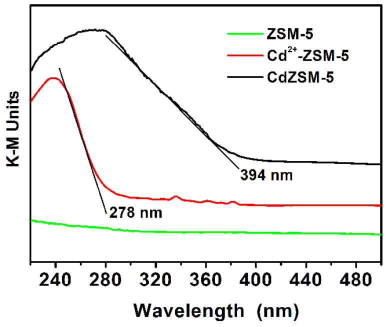

Fig. 4 UV/Vis diffuse reflectance spectra for the samples of ZSM-5, Cd^{2+}-ZSM-5 and CdZSM-5 (K-M Units = Kubella-Munk units).

UV-vis diffuse reflectance spectra were conducted for the samples of pristine ZSM-5, ion-exchanged Cd^{2+}-ZSM-5 and CdZSM-5 to analysis the transition of electrons. As shown in the UV-vis spectra (Fig. 4), pristine ZSM-5 zeolite does not exhibit significant absorption; but the ion-exchanged Cd^{2+}-ZSM-5 sample shows an absorption threshold at approximately 278 nm, which can be attributed to the O (2p) to Cd (5s) charge-transfer (CT) transition.[26, 27] In comparison with the Cd^{2+}-ZSM-5 sample, the UV-vis diffuse reflectance spectrum of the CdZSM-5 material shows a very broad band with the absorption threshold at 394 nm, which is consistent with the results of previously-reported transition of delocalized electrons.[6] This optical absorption between 394 and 278 nm can further support the presence of extra electrons on the framework of the as-prepared CdZSM-5 materials. Under the UV irradiation, the CdZSM-5 material is excited and some of the extra electrons are promoted from the delocalized positions to the Cd^{2+} cations, resulting in generation of Cd^+ species.

The electrons transfer capacities of the CdZSM-5 material can also be observed between the zeolite framework and the outside gas of O_2. As shown in Fig. 5a, after exposure to O_2 under the room temperature, EPR signals with g values of approximately 2.001 and 2.008, characteristic of superoxide (${}^{\bullet}O_2^-$) radicals are observed for the CdZSM-5 material,[28] indicating the occurrence of electron transfer between the zeolite framework and the outside oxygen molecules. It is speculated that the electrons delocalized on the CdZSM-5 framework are transferred to the O_2 molecules, generating ${}^{\bullet}O_2^-$ radicals associated with the zeolite ZSM-5. For comparison, the samples of pristine ZSM-5 and ion-exchanged Cd^{2+}-ZSM-5 after exposure to O_2 were also tested by the EPR spectra under the same condition (Fig. 5a). However, no EPR signal appears for the pristine ZSM-5 and ion-exchanged Cd^{2+}-ZSM-5 samples, indicating that no electron transfer between the zeolite framework and the Cd^{2+} cations occurs.

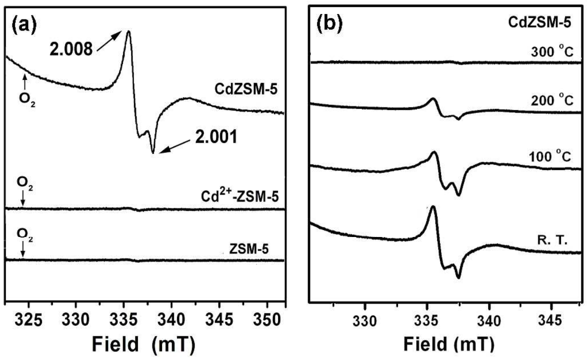

Fig. 5 *In situ* EPR specta for the samples of (a) pristine ZSM-5, Cd^{2+}-ZSM-5, and CdZSM-5 after exposure to O_2 under the room temperature, and (b) the ${}^{\bullet}O_2^-$-CdZSM-5 sample at different temperature.

$$\mathrm{CdZSM\text{-}5} + O_2 \underset{\Delta}{\overset{\text{R. T.}}{\rightleftharpoons}} {}^{\bullet}O_2^- \text{-CdZSM-5} \qquad (2)$$

It is found the thermal stability of the ${}^{\bullet}O_2^-$ radicals associated with the zeolite ZSM-5 is quite high. As shown in Fig. 5b, the EPR signals of ${}^{\bullet}O_2^-$ radicals are clearly observed under the room temperature. Increasing the temperature to 200 ºC, the EPR signals of ${}^{\bullet}O_2^-$ radicals are still observed. But once the temperature is over 300 ºC, the signals of ${}^{\bullet}O_2^-$ radicals are disappeared, indicating that ${}^{\bullet}O_2^-$ radicals are completely destroyed. As detected by gas-chromatography (GC), O_2 molecules are released [eqn (2)] (Fig. S4, ESI†). It is assumed that under the relatively high temperature of 300 ºC, all of the ${}^{\bullet}O_2^-$ radicals can dissociate from the zeolite to form O_2 molecules, leaving surplus electrons delocalization in the framework. After the removal of the ${}^{\bullet}O_2^-$ radicals, the Cd^+ species can be re-generated when the electron-rich cadmium-containing zeolite ZSM-5 is subjected to UV irradiation under room temperature (Fig. S5, ESI†). For comparison, pristine ZSM-5 and ion-exchanged Cd^{2+}-ZSM-5 after exposure to O_2 were also tested by the EPR spectra at different temperature (Fig. S6, ESI†), no EPR signal appears for these two samples, indicating that the transition of electrons can not happen between the zeolite and O_2 molecules.

Table 1 The results of oxygen storage experiment for the samples of ZSM-5, Cd^{2+}-ZSM-5 and CdZSM-5.

	Sample	Amount of evolved O_2 [a]	O_2 Storage Capacity
1	ZSM-5 (0.5 g)	1.2 μmol	2.4 μmol g^{-1}
2	Cd^{2+}-ZSM-5 (0.5 g)	4.9 μmol	9.8 μmol g^{-1}
3	CdZSM-5 (0.5 g)	160.5 μmol	321 μmol g^{-1}

[a] the amount of O_2 released was measured at 300 ºC.

The CdZSM-5 materials with lots of delocalized electrons can be used as ${}^{\bullet}O_2^-$ radicals reservoir. By controlling the temperature, the ${}^{\bullet}O_2^-$ radicals associated with the zeolite are able to turn into O_2. An oxygen storage/release experiment was designed for the pristine ZSM-5, Cd^{2+}-ZSM-5 and CdZSM-5 samples. First, the O_2 gas (> 99.999 %) was dried by passing through a column containing zeolite 4A to remove moisture. In a glove box filled with Ar, the samples were transferred into the glass tube reactor. Before introducing pure O_2, the reactor was evacuated to remove the Ar gas. O_2 was then introduced into the glass tube reactor slowly and reacted to the samples under the room temperature. Afterwards, the reactor was heated at 300 ºC and the amount of O_2 released was directly measured by GC. As shown in Table 1, the amount of evolved O_2 is approximately 321 μmol per gram of the CdZSM-5 sample, revealing their superior O_2 storage capacity. But the amounts of O_2 released for the pristine ZSM-5 and Cd^{2+}-ZSM-5 materials are only 2.4 and 9.8 μmol per gram of samples, respectively, revealing their poor storage capacities. These results indicate that O_2 storage capacity of the CdZSM-5 material containing delocalized electrons is far higher than that of the pristine ZSM-5 and Cd^{2+}-ZSM-5 materials. More importantly, after the removal of the oxygen molecules at 300 ºC, the oxygen storage capacity of the CdZSM-5 material is regained under the room temperature for the existence of extra electrons. The performance of the CdZSM-5 materials for oxygen storage was tested four cycles, and the results indicate that this material may be used repeatedly without noticeable deactivation (Fig. S6, ESI†). After the repeated tests, the crystal structure of the zeolite material remained intact, as judged by powder X-ray diffraction (Fig. S7, ESI†). Therefore, we speculate this electron-rich cadmium-modified ZSM-5 material can be used as good $^{\bullet}O_2^-$ radicals reservoir for the reactions that radicals and *in-situly* generated highly active O_2 are essential.

In summary, we demonstrate that in an electron-rich cadmium-modified zeolite there exist divalent cadmium cations partly accompanied by extra electrons delocalized over the zeolite framework in their vicinity. Under the UV irradiation, these delocalized electrons are promoted to the Cd^{2+} cations in the vicinity to form Cd^+ species. Meanwhile, this electron-rich cadmium-modified zeolite is considered as a good $^{\bullet}O_2^-$ radicals reservoir. The maximum oxygen storage amount can reach as high as 321 μmol per gram of the Cd-containing zeolite. With the temperature evaluated to 300 ºC, the $^{\bullet}O_2^-$ radicals associated with the zeolite can be dissociated from the zeolite to form O_2 molecules, leaving surplus electrons delocalization again over the zeolite framework. The storage of O_2 molecules using electron-rich Cd-containing zeolite is of significance in practical aspect. Our research on the successful preparation of electron-rich cadmium-modified zeolite and the exploitation of the delocalized electrons in the zeolite material open a new way for the encapsulation of O_2.

Acknowledgements

This work was financially supported by China Postdoctoral Science Foundation (2014M561455) and the National Natural Science Foundation of China (NSFC). The authors thank Prof. Jian-Qiang Wang and Dr. Hong-Liang Bao for helpful assistance in the XAFS measurements. The authors also thank Shanghai Synchrotron Radiation Facility for providing beam time (BL14W1).

Notes and references

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† Electronic Supplementary Information (ESI) available: Materials and experimental details, XRD and *In Situ* EPR spectra results of the materials. See DOI: 10.1039/c0xx00000x/

1 L. Tosheva and V. P. Valtchev, *Chem. Mater.*, 2005, **17**, 2494-2513.
2 K. B. Yoon, *J. Chem. Soc., Chem. Commun.*, 1988, **8**, 510-511.
3 K. Seff, *J. Phys. Chem. B*, 2005, **109**, 13840-13841.
4 P. Weis, P. R. Kemper and M. T. Bowers, *J. Phys. Chem. A*, 1997, **101**, 2809-2816.
5 J. A. Rabo, C. L. Angell, P. H. Kasai and V. Schomaker, *Discuss. Faraday Soc.*, 1966, **41**, 328-349.
6 L. Li, G. D. Li, C. Yan, X. Y. Mu, X. L. Pan, X. X. Zou, K. X. Wang and J. S. Chen, *Angew. Chem. Int. Ed.*, 2011, **50**, 8299-8303.
7 J. F. Wang, K. X. Wang, J. Q. Wang, L. Li and J. S. Chen, *Chem. Commun.*, 2012, **48**, 2325-2327.
8 J. F. Wang, K. X. Wang, J. Q. Wang, L. Li, Y. M. Jiang, X. X. Guo and J. S. Chen, *J. Solid State Chem.*, 2013, **202**, 111-115.
9 V. V. Krishnan, S. L. Suib, D. R. Corbin, S. Schwarz and G. E. Jones, *Catal. Today*, 1996, **31**, 199-205.
10 V. V. Krishnan, S. L. Suib, D. R. Corbin, S. Schwarz and G. E. Jones, *Chem. Commun.*, 1996, 395-396.
11 G. E. Pavlovskaya, C. D. Ren, M. Van Buskirk, C. Dybowski, D. R. Corbin, J. A. Reimer and A. T. Bell, *Catal. Lett.*, 2002, **80**, 19-24.
12 J. Li, E. D. Wu, C. J. Geng and X. M. Du, *Prog. Chem.*, 2010, **22**, 2238-2247.
13 E. Y. Choi, S. H. Lee, Y. Kim, Y. W. Han and K. Seff, *J. Phys. Chem. B*, 2002, **106**, 7569-7573.
14 T. Sprang, A. Seidel, M. Wark, F. Rittnera and B. Boddenberga, *J. Mater. Chem.*, 1997, **7**, 1429-1432.
15 D. Meyerstein and W. A. Mulac, *Inorg. Chem.*, 1970, **9**, 1762-1766.
16 A. Goldbach, P. Barker, P. Anderson and P. Edwards, *Chem. Phys. Lett.*, 1998, **292**, 137-142.
17 B. D. Cutforth, R. J. Gillespie and P. K. Ummat, *Rev. Chim. Miner.*, 1976, **13**, 119.
18 H. Garcia and H. D. Roth, *Chem. Rev.*, 2002, **102**, 3947-4007.
19 L. Li, X. S. Zhou, G. D. Li, X. L. Pan and J. S. Chen, *Angew. Chem. Int. Ed.*, 2009, **48**, 6678-6682.
20 D. Grandjean, H. L. Castricum, H. L. van den Heuvel and B. M. Weckhuysen, *J. Phys. Chem. B*, 2006, **110**, 16892-16901.
21 A. Mijovilovich and W. Meyer-Klaucke, *J. Synchrotron Rad.*, 2003, **10**, 64-68.
22 I. F. Vasconcelos, E. A. Haack, P. A. Maurice and B. A. Bunker, *Chem. Geol.*, 2008, **249**, 237-249.
23 M. Grafe, B. Singh and M. Balasubramanian, *J. Colloid Interface Sci.*, 2007, **315**, 21-32.
24. M. G. Burnett, C. Hardacre, J. M. Mallon, H. J. Mawhinney and R. M. Ormerod, *Phys. Chem. Chem. Phys.*, 2000, **2**, 1273-1279.
25 A. V. Egranov, E. A. Radzhabov, V. F. Ivashechkin, M. A. Semenova and I. E. Vasil'eva, *J. Phys.: Condens. Matter.*, 2008, **20**, 465213.
26 S. Vasireddy, K. W. Street and H. B. Mark Jr, *Anal. Chem.*, 1981, **53**, 868-873.
27 T. Sprang and B. Boddenberg, *Appl. Magn. Reson.*, 1995, **8**, 415-425.
28 A. F. Bedilo, M. A. Plotnikov, N. V. Mezentseva, A. M.Volodin, G. M. Zhidomirov, I. M. Rybkina and K. J. Klabundeb, *Phys. Chem. Chem. Phys.* 2005, **7**, 3059-3069.

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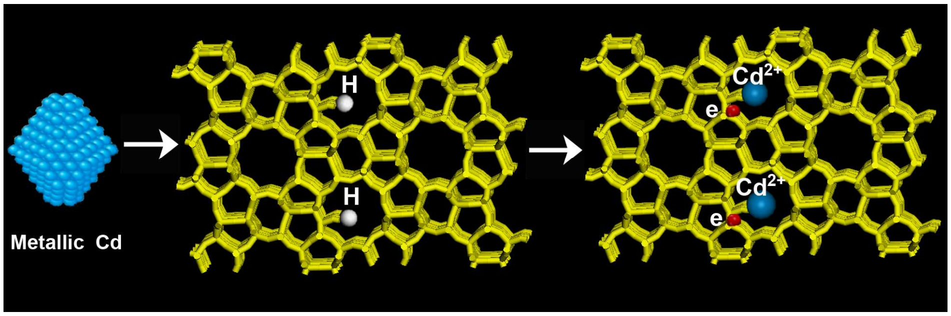

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