Dalton Transactions

COMMUNICATION

RSCPublishing

View Article Online View Journal | View Issue

Cite this: Dalton Trans., 2013, 42, 9423

Received 20th March 2013, Accepted 16th April 2013

DOI: 10.1039/c3dt50747e

www.rsc.org/dalton

A cobalt-based 3D porous framework with excellent catalytic ability for the selective oxidation of *cis*-cyclooctene[†]

Guangju Zhang, Hao Li, Fangfang Zhao, Hailiang Hu,* Hui Huang, Haitao Li, Xiao Han, Ruihua Liu, Huan Dong, Yang Liu* and Zhenhui Kang*

A 3D porous framework $[Co_3(\mu_2-OH)_4(I)_2]\cdot 2H_2O$ (I = hypoxanthine) with two types of 1D channels possess excellent catalytic ability for the selective oxidation of *cis*-cyclooctene.

Porous coordination polymers (PCPs) or metal–organic frameworks (MOFs) with designable framework structures have attracted great attention from both industry and academia¹ due to their potential applications as functional solid materials in the fields of fuel gas storage,² catalysis³ magnetism⁴ and separation.⁵ Notably, the size, shape, dimensions and surface functionality of the nanochannels can be systematically tuned by changing the combination of organic ligands and metal ions.^{1b,6} In this field, Yaghi,⁷ Kitagawa,⁸ Long,⁹ Férey,¹⁰ Zhou,¹¹ Chen¹² and Qiu¹³ *et al.* have reported much work and gained fruitful results, in which various PCPs/MOFs were wildly investigated covering adsorption, separation, polymerization as well as heterogeneous catalysis.

Catalysis is a core issue of chemistry and plays a significant role in current chemical industry, as well as environmental and energy problems. Furthermore, oxidation is an important method for the synthesis of chemical intermediates in the manufacture of high-tonnage commodities, high-value fine chemicals, agrochemicals and pharmaceuticals. The introduction of catalytic systems using oxygen from air is preferred for 'green' processing. Alkene selective oxidation has attracted much attention because of the related products of epoxides are valuable and resourceful commercial intermediates. For example, many kinds of catalysts (such as hybrid-POMs,¹⁴ T-molecular sieves,¹⁵ metal porphyrins,¹⁶ Au, Co, Fe, Ti, Ru,¹⁷ high-valence metal-organic compounds (Mo(vI), W(vI), and Re(vII) complexes),¹⁸ and carbon and silicon nanoparticles)¹⁹ been developed for the selective oxidation of have

cis-cyclooctene. However, they usually suffer from low conversion efficiency, unsatisfactory selectivity and poor stability of catalyst. 18f

The activity and selectivity of a catalytic reaction can be tuned by varying the size, composition and morphology of inorganic-solid catalysts. Besides those inorganic species, PCPs/ MOFs can also act as important catalysts, which are similar to heterogeneous catalysts and also allowed for easier post-reaction separation and recyclability than homogeneous catalysts. General speaking, in heterogeneous catalysis, PCPs/MOFs usually act as the carriers for an active mass, fix the catalytically active species, and realize the formation and stabilization of coordination species in the framework.^{20–23} Although PCPs/ MOFs could be used as catalysts with high catalytic activity in various reactions^{20,23a,24–28} (such as, cyanosilylation, hydrogenation, polymerization, oxidation, and isomerization), there still lacks the studies on their application in hydrocarbon selective oxidation reactions (using *t*-BuOOH as oxidant).³

Here we report a 3D PCP, namely $[Co_3(\mu_2-OH)_4(I)_2]\cdot 2H_2O$ (compound **1**, I = hypoxanthine; this structure was also reported in ref. 29), exhibiting an unprecedented 3D porous framework containing two types of 1D channels running along *c* axis. In ref. 29, the magnetism property of compound **1** is fully investigated, while here we studied the catalytic ability of compound **1**. The catalytic experiments showed that compound **1**, directly used as heterogeneous catalyst without any supports, indeed possesses excellent catalytic ability for the selective oxidation of *cis*-cyclooctene (34.84% conversion based on *cis*-cyclooctene and 87.71% selectivity for epoxycyclooctane).

In our experiments, $[Co_3(\mu_2-OH)_4(I)_2]\cdot 2H_2O$ (1)[‡] was synthesized under hydrothermal conditions by using a mixture of $Co(OAC)_2\cdot 4H_2O$, hypoxanthine, NaOH aqueous solution and distilled water at 130 °C for 4 days. Crystal structure analysis reveals that compound **1** consists of three Co^{II} ions, two hypoxanthine anions, four μ_2 -OH anions, and two water molecules (Fig. 1a). In compound **1**, there are two crystallographically independent atoms (Co1, Co2), which exhibit two kinds of coordination geometries. The Co1 atoms display distorted octahedral geometry of $[Co_{(1)}N_2O_4]$, being coordinated by two

Institute of Functional Nano & Soft Materials (FUNSOM) and Jiangsu Key Laboratory for Carbon Based Functional Materials & Devices, Soochow University, Suzhou, Jiangsu, 215123, P. R. China. E-mail: zhkang@suda.edu.cn, yangl@suda.edu.cn, hlhu@suda.edu.cn; Fax: +86-512-65882846; Tel: +86-512-65880957

[†]Electronic supplementary information (ESI) available: Figures, XRPD, IR, TG, CIF files and scheme, together with tables. CCDC 917476. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt50747e



Fig. 1 (a) Ball-stick view of the asymmetric unit of **1**. (b, c) Stick and polyhedral view of the 1D Co–O–Co chain running along the c axis. (d) Stick and polyhedral view of the 3D porous framework. (e) The novel (3,8)-connected network with a $(3.5^2)(3^4.4^3.5^{7.6^{11}.7^3})$ topology. (f) The left- and right-handed helical water chains along the c axis.

oxygen atoms from two hypoxanthine ligands and two aqua ligands in the equator plane, as well as two nitrogen atoms from two hypoxanthine ligands at the axial sites. Whereas each Co2 center is ligated by one oxygen atom of hypoxanthine ligand and three aqua ligands to complete a distorted octahedral geometry of $[Co_{(2)}N_2O_4]$. In 1, each $[Co_{(1)}N_2O_4]$ octahedral is connected to two $[Co_{(2)}N_2O_4]$ octahedrals in ABA sequence by edge-sharing oxygen atoms (O1w, O9) to form a trinuclear cobalt cluster, which are further connected to each other by edge-sharing oxygen atoms (O2w, O2w') mode to form an infinite 1D Co-O-Co chain running along the *c* axis (Fig. 1b and 1c). The adjacent 1D chains are further interconnected by the hypoxanthine ligands to produce a 2D layer in the bc plane (Fig. S1[†]). Simultaneously the hypoxanthine ligands act as ligaments to join the adjacent 2D sheets together, generating a 3D porous network (Fig. 1d and Fig. S2⁺). Further detailed structural analysis show that two types of 1D channels are present within the framework. As shown in Fig. 1d and 1e, the typical regular square (type-A and type-B) channels exhibit the sizes of 11.2 × 11.2 and 8.5 × 8.5 Å, respectively.

Another note worthy aspect of **1** is the helical chains formed with free water molecules (O3W). The adjacent water molecules, located in the type-A channel, are bonded to each other through hydrogen bonding (O3W…H3B…O3W = 2.856(8)Å) to produce left- and/or right-handed helical water chains with a pitch of 8.45 Å along the *c* axis (Fig. 1f), in which the O3W molecule acts as an acceptor as well as a donor. Here water–water interactions are important for the stability of the overall structure. Moreover, such water chains have attracted much interest due to the occurrence in many fundamental biological processes.^{30–32}

From a topological perspective, each hypoxanthine ligand is linked to three trinuclear cobalt clusters that can be reduced to a three-connected node; each trinuclear cobalt cluster is surrounded by six hypoxanthine ligands and two other trinuclear cobalt clusters that can be simplified as a eight-connected node (Fig. S3†). Therefore, the 3D porous framework can be rationalized as a binodal (3,8)-connected network with a $(3.5^2)(3^4.4^3.5^7.6^{11}.7^3)$ topology (Fig. 1e).

Based on the TG analyses (ESI[†]), the crystal sample was dried under a high vacuum at 150 °C for 10 h to remove the lattice water. For 1, PLATON³³ analysis shows that the effective free void is about 30.7% of the crystal volume (1114.8 Å³ out of the 3634.1 Å³ unit-cell volume). In order to testify the porous structure of 1, the N₂ and CO₂ sorption isotherms were performed at 77 and 195 K on the activated samples, respectively. The adsorption isotherms of N₂ and CO₂ display a steep rise at the low relative pressure region, and the isotherms can be categorized as type I, indicating a typical physisorption process of a microporous material. As shown in Fig. 2a, the activated sample 1 adsorbs N₂ and CO₂ of 237.4 and 160.4 cm³ g⁻¹ at



Fig. 2 (a) Nitrogen and carbon dioxide adsorption–desorption isotherms of **1** at 77 and 195 K, respectively. (b) Thermal variation of χ_M and $\chi_M T$ for **1**. Insert: plot of thermal variation of χ_M^{-1} for **1**.

View Article Online

Communication

1 atm, respectively. The selective adsorption behavior of N_2 over CO_2 is attributed to there being no large polarizability and quadrupole moment of CO_2 interacting with the hydrophobic pore surface and can not make a contribution to the potential energy of adsorption.

The structural motif of the framework consists of the infinite 1D Co-O-Co chain formed by the trinuclear cobalt clusters, in which the $[Co_{(1)}N_2O_4]$ octahedra are connected to two $[Co_{(2)}N_2O_4]$ octahedra by edge-sharing oxygen atoms. Therefore, the magnetic susceptibility of 1 is further investigated over the temperature range 2-300 K at an applied field of 1 kOe and is shown as $\chi_M T$ and χ_M versus T plots in Fig. 2b. At 300 K, the $\chi_{\rm M}T$ value of 9.353 cm³ K mol⁻¹ (8.650 $\mu_{\rm B}$) is much higher than the spin-only value of 0.439 cm³ K mol⁻¹ (1.874 $\mu_{\rm B}$) expected for one isolated Co^{II} ion (S = 3/2, g = 2.0), which can be ascribed to the strong orbital contribution to the magnetic moment of Co^{II} centers.^{4,34} Upon cooling, the $\chi_{\rm M}T$ value decreases monotonically and tends to zero at low temperature (the $\chi_M T$ value of 0.439 cm³ K mol⁻¹ at 2 K), while the χ_M value increases to a rounded maximum of 0.548 cm³ mol⁻¹ at ca. 9.5 K and then drops rapidly. The Curie–Weiss fitting of $1/\chi_{M}$ in the temperature range of 10-300 K gives a good result with $C = 9.678 \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = -11.191 \text{ K. X.-M. Zhang et al.}$ have done a detailed study on the magnetism property of 1, which shows rare metamagnetic behavior.²⁹

Considering that cobalt plays an important role in current petrochemical and plastic industries, as both a hetero and homogeneous catalyst.³⁵⁻³⁹ In the following experiments, the catalytic performance of 1 for the selective oxidation of ciscyclooctene is further studied, cis-cyclooctene (10 mL) and asfabricated catalysts (compound 1, 20 mg) were added to 50 mL round bottom flask with water condenser and continuous magnetic stirring. Then 0.5 mL tert-butyl hydroperoxide (TBHP), used as initiator, was added dropwise to the system free of solvent. At last, the mixture was stirred under relatively mild conditions (80 °C, 24 h, and atmospheric pressure). The oxidation products were analyzed by gas chromatography (GC) and gas chromatography-mass spectroscopy (GC-MS). The catalytic ability of 1 was investigated for oxidation of cis-cyclooctene in the absence of solvent using TBHP as radical initiator and oxygen (in air) as oxidant at 80 °C (Scheme S1⁺). The detailed conversion of cis-cyclooctene and selectivity of oxidation products are shown in Table S1.[†] Fig. 3 demonstrates the catalytic performance of 1 for the selective oxidation of cis-cyclooctene, which reveals that the percentage of conversion and the selectivity reach 17.97% and 80.78% after 12 h, respectively. After 24 h reaction, high conversion efficiency of 34.84% and high selectivity up to 87.71% are achieved simultaneously. Both the conversion of cis-cyclooctene and the selectivity of epoxycyclooctane increase with time going. At the same time, the selectivity of 1,2-cyclooctanediol falls to 3.71% from 11.47%. Similarly, the selectivity of cycloocten-2-one falls to 7.82% from 14.41%.

In our followed catalytic experiments, after the first catalytic run, the catalyst (compound 1) was separated from the reaction solution, washed several times with dichloromethane to



Fig. 3 The relationship between the conversion of *cis*-cyclooctene/selectivity of different products and reaction time with compound 1 as catalyst.

remove the physisorbed molecules, dried and reused in another catalytic cycle. A series of catalytic experiments suggested that, as catalyst, compound **1** was stable (X-ray powder diffraction patterns, XRPD, see Fig. S5†) and still kept catalytic activity (with nearly constant conversion and selectivity, see Fig. S6†) after five catalytic cycles. Further blank reactions (*i.e.*, without catalyst) did not result in any epoxide and/ or other products being produced. Moreover, the filtrate solution test (additional 24 h reaction after removing the compound **1** from the reaction medium) showed no catalytic activity, which indicated that the leaching does not seem to play an important role in present systems.⁴⁰ All above-mentioned catalytic experiments show that compound **1** indeed acts as a heterogeneous catalyst in the present catalytic system.

Based on all above results and discussion, we propose the mechanism of this catalytic reaction as follows. In compound 1, the divalent cobalt ions have been coordinated with waters that can be readily removed, which retain free coordination sites that are readily accessible for oxidants and/or active site for the generation of radicals (such as active oxygen radicals).^{1e} Also, TBHP acts as a free radical initiator with oxygen in air as the oxidant, while the C=C bond is directly oxidized by a per-oxide species generated from the radical initiator and oxygen.^{17a,19b} Here we also need to further point out that, the present catalyst system is endued with the structure tunable ability, and then their catalytic abilities may further be improved by using different organic ligands (1,3,5-benzene-tricarboxylate acid, terephthalic acid *etc.*) and metals (Cu, Zn, Mn *etc.*).

In summary, a 3D porous framework with two types of 1D channels has been constructed by the hypoxanthine ligand and cobalt salt. The catalytic experiment indicates that compound **1**, directly used as a heterogeneous catalyst without any supports, possess excellent catalytic ability for the selective oxidation of *cis*-cyclooctene. Considering that there are a large number of possible organic ligands and metal ions that can be used in this synthetic strategy, the results presented here may

open a promising route for the design and fabrication of other novel PCPs/MOFs with high catalytic performance.

This work is supported by the National Basic Research Program of China (973 Program) (2012CB825803, 2013CB932702), the National Natural Science Foundation of China (51132006, 21073127, 21071104), the Specialized Research Fund for the Doctoral Program of Higher Education (20123201110018), a Suzhou Planning Project of Science and Technology (ZXG2012028), a Foundation for the Author of National Excellent Doctoral Dissertation of China (200929), and a project funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions.

References

‡Experimental data for 1: a mixture of Co(OAC)₂·4H₂O (0.6 mmol), hypoxanthine (0.6 mmol), NaOH aqueous solution (0.6 mL, 1 M) and distilled water (10 mL) was placed in an 18 mL Teflon-lined stainless steel vessel and stirred about 15 min in air. The vessel was sealed and heated at 130 °C for 4 d under autogenous pressure, and then cooled to room temperature naturally. Purple block crystals of 1 were obtained (60% yield based on Co). Elemental analysis (%) calcd for C₁₀H₁₄Co₃N₈O₈ (551.08): C, 21.80; H, 2.56; N, 20.33%. Found: C, 21.76; H, 2.60; N, 20.30%. FT-IR (KBr): $\dot{\nu}$ = 3516(s), 3405(s), 3197(m), 3055(m), 3003(m), 2923(w), 2873(w), 1659(s), 1560(s), 1595(m), 1535(m), 1441(m), 1406(m), 1387(m), 1350(m), 1303(m), 1290(m), 1259(m), 1190(m), 1167(m), 1124(m). Crystal data for 1: C₁₀H₁₄Co₃N₈O₈, tetragonal, space group *I*4₁/*a*, *a* = *b* = 20.7387(5), *c* = 8.4495(4) Å, $\alpha = \beta = \gamma = 90^{\circ}$. *V* = 3634.1(2), *Z* = 8, *T* = 296(2) K, R_{int} = 0.0266, R₁ [*I* > 2 σ (*I*)] = 0.0371, wR₂ (all data) = 0.1592, 2237 unique reflections, GOF = 1.011.

- (a) C. Janiak, Dalton Trans., 2003, 2781; (b) S. Kitagawa,
 R. Kitaura and S. Noro, Angew. Chem., Int. Ed., 2004, 43, 2334; (c) A. U. Czaja, N. Trukhan and U. Müller, Chem. Soc. Rev., 2009, 38, 1284; (d) Z. Yin and M. H. Zeng, Sci. China. Chem., 2011, 54, 1371; (e) L. Ma, C. Abney and W. Lin, Chem. Soc. Rev., 2009, 38, 1248.
- 2 M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469.
- 3 (a) C. D. Wu, A. Hu, L. Zhang and W. B. Lin, J. Am. Chem. Soc., 2005, 127, 8940; (b) S. H. Cho, B. Q. Ma, S. T. Nguyen, J. T. Hupp and T. E. Albrecht-Schmitt, Chem. Commun., 2006, 2563; (c) M. J. Ingleson, J. P. Barrio, J. B. Guilbaud, Y. Z. Khimyak and M. J. Rosseinsky, Chem. Commun., 2008, 2680; (d) Y. Lu, M. Tonigold, B. Bredenkötter, D. Volkmer, J. Hitzbleck and G. Langstein, Z. Anorg. Allg. Chem., 2008, 634, 2411; (e) F. J. Song, C. Wang, J. M. Falkowski, L. Q. Ma and W. B. Lin, J. Am. Chem. Soc., 2010, 132, 15390.
- 4 M. Kurmoo, Chem. Soc. Rev., 2009, 38, 1353.
- 5 L. Pan, D. H. Olson, L. R. Ciemnolonski, R. Heddy and J. Li, *Angew. Chem.*, 2006, **118**, 632.
- 6 (a) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, 423, 705;
 (b) C. J. Kepert, *Chem. Commun.*, 2006, 695.
- 7 H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, E. Choi, A. Ö. Yazaydin, R. Q. Snurr, M. O'Keeffe, J. Kim and O. M. Yaghi, *Science*, 2010, **329**, 424.
- 8 T. Uemura, N. Yanaia and S. Kitagawa, *Chem. Soc. Rev.*, 2009, **38**, 1228.

- 9 L. J. Murray, M. Dincă and J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294.
- 10 G. Férey, Chem. Soc. Rev., 2008, 37, 191.
- 11 D. Zhao, D. J. Timmons, D. Q. Yuan and H. C. Zhou, Acc. Chem. Res., 2011, 44, 123.
- 12 (a) J. B. Lin, J. P. Zhang and X. M. Chen, J. Am. Chem. Soc., 2010, 132, 6654; (b) Y. B. Zhang, W. X. Zhang, F. Y. Feng, J. P. Zhang and X. M. Chen, Angew. Chem., Int. Ed., 2009, 48, 5287.
- 13 S. L. Qiu and G. S. Zhu, Coord. Chem. Rev., 2009, 253, 2891.
- 14 (a) N. K. Chika, H. Kunihiko, N. Satoshi and N. Keni, J. Mol. Catal. A: Chem., 2007, 262, 25; (b) F. X. Gao, R. M. Hua and T. Yamase, Chin. J. Catal., 2005, 26, 153; (c) C. Venturello, E. Alneri and M. Ricci, J. Org. Chem., 1983, 48, 3831.
- (a) M. G. Clerici and P. Ingllina, J. Catal., 1993, 140, 71;
 (b) H. X. Gao, G. X. Lu, J. S. Suo and S. B. Li, Appl. Catal., A, 1996, 138, 27;
 (c) F. W. Fan, Y. Q. Deng and F. Shi, J. Mol. Catal., 2003, 17, 465;
 (d) L. L. Wang, Y. M. Liu, W. Xie, H. J. Zhang, H. H. Wu, Y. W. Jiang, M. Y. He and P. Wu, J. Catal., 2007, 246, 205.
- 16 (a) C. Sandro and T. Umberto, Adv. Synth. Catal., 2001, 343, 819; (b) N. A. Stephenson and A. T. Bell, J. Am. Chem. Soc., 2005, 8, 635; (c) C. L. Ni, D. Q. Xu and Z. R. Yao, Chem. World, 1999, 4, 187.
- 17 (a) M. D. Hughes, Y. J. Xu, P. Jenkins, P. McMorn, P. Landon, D. I. Enache, A. F. Carley, G. A. Attard, G. J. Hutchings, F. King, E. H. Stitt, P. Johnston, K. Griffn and C. J. Kiely, *Nature*, 2005, 437, 1132; (b) R. Neumann and M. Dahan, *Nature*, 1997, 388, 353; (c) J. M. Thomas, *Angew. Chem., Int. Ed.*, 1999, 38, 3588; (d) M. J. Krishna, S. Jince and V. J. Raksh, *J. Mol. Catal. A: Chem.*, 2007, 274, 41; (e) Y. Shiraishi, M. Morishita and T. Hirai, *Chem. Commun.*, 2005, 977.
- (a) R. A. Sheldon and J. A. Van Doorn, J. Catal., 1973, 31, 427; (b) K. A. Jørgensen, Chem. Rev., 1989, 89, 431; (c) F. E. Kühn, A. M. Santos, I. S. Goncalves, C. C. Romão and A. D. Lopes, Appl. Organomet. Chem., 2001, 15, 43; (d) F. E. Kühn, A. M. Santos and M. Abrantes, Chem. Rev., 2006, 106, 2455; (e) F. E. Kühn, A. M. Santos and W. A. Herrmann, Dalton Trans., 2005, 2483; (f) F. E. Kühn, E. Herdtweck, J. J. Haider, W. A. Herrmann, I. S. Goncalves, A. D. Lopes and C. C. Romão, J. Organomet. Chem., 1999, 583, 3.
- (a) Z. H. Kang, Y. Liu and S. T. Lee, *Nanoscale*, 2011, 3, 777;
 (b) Z. H. Kang, C. H. A. Tsang, Y. Liu, D. D. D. Ma, N. B. Wong and S. T. Lee, *Chem. Commun.*, 2009, 5829;
 (c) H. Huang, H. C. Zhang, Z. Ma, Y. Liu, H. Ming, H. T. Li and Z. H. Kang, *Nanoscale*, 2012, 4, 4964.
- 20 S. De Rosa, G. Giordano, T. Granato, A. Katovic, A. Siciliano and F. Tripicchio, *J. Agric. Food Chem.*, 2005, **53**, 8306.
- 21 (a) U. Mueller, L. Lobree, M. Hesse, O. M. Yaghi and M. Eddaoudi, *Patent*, WO 03/101975, 2003; (b) U. Mueller, O. Metelkina, H. Junicke, T. Butz and O. M. Yaghi, *Patent*, US 2004/081611, 2004.
- 22 D. Jiang, T. Mallat, F. Krumeich and A. Baiker, *J. Catal.*, 2008, 257, 290.

- 23 (a) K. Schlichte, T. Kratzke and S. Kaskel, *Microporous Mesoporous Mater.*, 2004, 73, 81; (b) M. J. Ingleson, J. P. Barrio, J. Bacsa, C. Dickinson, H. Park and M. J. Rosseinsky, *Chem. Commun.*, 2008, 1287.
- 24 S. Hermes, M. K. Schröter, R. Schmid, L. Khodeir, M. Muhler, A. Tissler, R. W. Fischer and R. A. Fischer, *Angew. Chem., Int. Ed.*, 2005, 44, 6237.
- 25 L. Alaerts, E. Séguin, H. Poelman, F. Thibault-Starzyk, P. A. Jacobs and D. E. De Vos, *Chem.–Eur. J.*, 2006, **12**, 7353.
- 26 J. Perles, M. Iglesias, M. A. Martin-Luengo, M. A. Monge, C. Ruiz-Valero and N. Snejko, *Chem. Mater.*, 2005, 17, 5837.
- 27 (a) E. Guitérrez-Puebla, C. Cascales-Sedano, B. Gómez-Lor, M. M. Iglesias-Hernandez, M. A. Monge-Bravo, C. Ruiz-Valero and N. Snejko, *Patent*, ES 2,200,681, 2004; (b) B. Gómez-Lor, E. Guitérrez-Puebla, M. Iglesias, M. A. Monge, C. Ruiz-Valero and N. Snejko, *Inorg. Chem.*, 2002, **41**, 2429.
- (a) J. Perles, M. Iglesias, C. Ruiz-Valero and N. Snejko, J. Mater. Chem., 2004, 14, 2683; (b) F. X. Llabrés i Xamena, A. Abad, A. Corma and H. Garcia, J. Catal., 2007, 250, 294;
 (c) C. N. Kato and W. Mori, C. R. Chim., 2007, 10, 284;
 (d) F. X. Llabrés i Xamena, O. Casanova, R. Galiasso Tailleur, H. Garcia and A. Corma, J. Catal., 2008, 255, 220.
- 29 X. H. Zhang, Z. M. Hao and X. M. Zhang, *Chem.-Eur. J.*, 2011, 17, 5588.
- 30 S. Cukierman, Biophys. J., 2000, 78, 1825.
- 31 K. M. Jude, S. K. Wright, C. Tu, D. N. Silverman, R. E. Viola and D. W. Christianson, *Biochemistry*, 2002, **41**, 2485.

- 32 H. Kandori, *Biochim. Biophys. Acta, Bioenerg.*, 2000, **1460**, 177.
- 33 A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Untrecht University, 2003.
- 34 O. Kahn, Molecular Magnetism, VCH, New York, 1993.
- 35 (a) E. Iglesia, *Appl. Catal., A*, 1997, 161, 59; (b) R. Oukaci,
 A. H. Singleton and J. G. Goodwin, *Appl. Catal., A*, 1999,
 186, 129; (c) R. Bechara, D. Balloy and D. Vanhove, *Appl. Catal., A*, 2001, 207, 343; (d) E. V. Steen and F. F. Prinsloo, *Catal. Today*, 2002, 71, 327.
- 36 (a) A. Tavasoli, Y. Mortazavi, A. Khodadadi and K. Sadagiani, *Iran. J. Chem.Chem. Eng.*, 2005, 35, 9;
 (b) P. J. Van Berge, J. Van De Loosdrecht, S. Barradas and A. M. Van Der Kraan, *Catal. Today*, 2000, 58, 321;
 (c) G. Jacobs, T. K. Das, Y. Zhang, J. Li, G. Racoillet and B. H. Davis, *Appl. Catal.*, A, 2002, 233, 263.
- 37 R. M. Thomas, P. C. B. Widger, S. M. Ahmed, R. C. Jeske,
 W. Hirahata, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2010, 132, 16520.
- 38 D. K. Zhong and D. R. Gamelin, J. Am. Chem. Soc., 2010, 132, 4202.
- 39 (a) J. A. Schwarz, C. Contescu and A. Contescu, *Chem. Rev.*, 1995, 95, 477; (b) M. K. Gnanamani, G. Jacobs, U. M. Graham, W. Ma, V. R. R. Pendyala, M. Ribeiro and B. H. Davis, *Catal. Lett.*, 2010, 134, 37.
- 40 M. Abrantes, A. Sakthivel, C. C. Romão and F. E. Kühn, *J. Organomet. Chem.*, 2006, 691, 3137.