A Ni_3O-cluster based porous MOF for catalytic conversion of CO_2 to cyclic carbonates

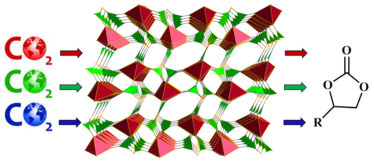
Yang Yang, Zhenli Guo, Xiao-Hong Chen, Jinglin Liu

PII: S0022-4596(19)30235-X
DOI: https://doi.org/10.1016/j.jssc.2019.05.010
Reference: YJSSC 20753

To appear in: *Journal of Solid State Chemistry*

Received Date: 26 March 2019
Revised Date: 7 May 2019
Accepted Date: 8 May 2019

Please cite this article as: Y. Yang, Z. Guo, X.-H. Chen, J. Liu, A Ni_3O-cluster based porous MOF for catalytic conversion of CO_2 to cyclic carbonates, *Journal of Solid State Chemistry* (2019), doi: https://doi.org/10.1016/j.jssc.2019.05.010.


CO2
CO2
CO2
O
O
O
R

A Ni_3O-cluster based porous MOF for catalytic conversion of CO_2 to cyclic carbonates

Yang Yang,[*] Zhenli Guo, Xiao-Hong Chen, Jinglin Liu

Inner Mongolia Key Lab of Carbon Nanomaterials, Nano Innovation Institute (NII), College of Chemistry and Chemical Engineering, Inner Mongolia University for the Nationalities (IMUN), Tongliao 028000, People's Republic of China.

E-mail addresses: yangyang-000@163.com

Abstract

A novel Ni_3O-based MOF, $\{[Ni_3HL(\mu_3\text{-}OH)(H_2O)_2]\cdot 3(H_2O)\cdot DMA\}_n$ (**1**), was constructed based on an organosilicon hexacarboxylic acid linker of 5,5',5''-(methylsilanetriyl)triisophthalic acid (H_6L). In this structure, the deprotonated carboxylate groups assemble with trinuclear metal cluster nodes to give a 6-connected uninodal net. It possesses open channels and rich metal sites, and displays CO_2 adsorption behavior. Further investigations indicate that the compound is catalytically effective for the cyclic carbonates by cycloaddition of CO_2 to epoxides. Besides, the catalyst could be reused 5 times with no significant loss of catalytic activity and without structural deterioration**.**

Keywords: metal cluster; CO_2 adsorption; CO_2 cycloaddition; catalyst

1. Introduction

There has been an increasing research interest in CO_2 capture, storage and utilization, due to awareness of a rapid growth in CO_2 emission in the atmosphere and the consequent global warming [1]. Efficient transformation of CO_2 into valuable chemicals in the catalysis is very attractive both academically and industrially, because CO_2 is an abundant C1 building block in organic synthesis and is recognized to be inexpensive and renewable [2]. The cost-effective procedures have been developed by forming C-C, C-N, C-O and C-H bonds to convert CO_2 into value-added chemicals [3–6]. However, because CO_2 molecules possess thermodynamic stability and kinetic inertness, efficient chemical fixation of CO_2 remains difficult under mild conditions. In order to overcome such barriers, a relatively high free energy is essential for a reaction. In this area, coupling of CO_2 and epoxide to cyclic carbonates presents one of the most promising methodologies [7-9]. Moreover, the addition of CO_2 to epoxides is a 100% atom-efficient reaction with no by-products. The produced cyclic carbonate is widely used as polar aprotic solvent, electrolyte, and raw material for polycarbonate [10].

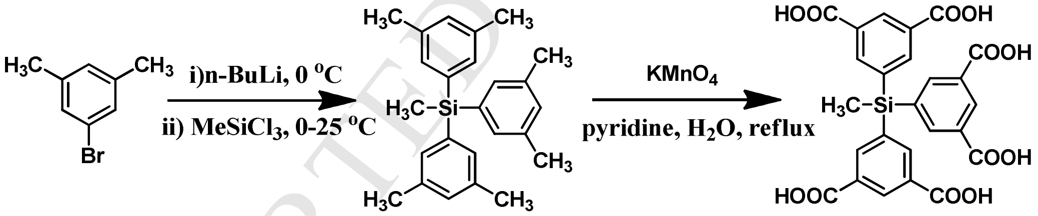
Homogeneous and heterogeneous catalysts are two main classes of catalytic systems developed for this CO_2 transformation. Homogeneous systems are accepted to be effective, but generally undergo a complicated separation of the catalysts from the reaction product [11-13]. Several types of heterogeneous catalysts have been applied to the chemical fixation of CO_2 to form cyclic carbonate [14-16]. However, many catalysts suffer from an inhomogeneous distribution of active sites that reduce product selectivity [17]. Metal-organic frameworks (MOFs), a class of crystalline porous solids with infinite networks built from inorganic metal ions/cluster and organic linkers [18-21], have been demonstrated to be promising heterogeneous catalysts in various reactions [22-24]. On basis of the relationship between the function of MOFs and modular nature at the molecular level, decorating the pore environment with rich Lewis acidic sites can endow them with desirable catalytic activity [25]. Focusing on the above considerations, a metal cluster-based MOF could be an ideal candidate for CO_2 conversion with epoxides in virtue of the more active sites compared with the single metal center at the node.

In this work, a novel porous MOF of $\{[Ni_3HL(\mu_3\text{-}OH)(H_2O)_2]\cdot 3(H_2O)\cdot DMA\}_n$ **1** (DMA = N,N'-dimethylacetamide) was obtained under solvothermal condition. Compound **1** is built from inorganic Ni_3-O cluster and organic steric linker of 5,5',5''-(methylsilanetriyl)triisophthalic acid (H_6L). With open channels and rich metal sites, the compound exhibits CO_2 capture and conversion under mild reaction condition. Its catalytic activity is greatly superior to most MOF-based catalysts, and its structure as heterogeneous catalyst can be recycled at least five runs without a significant compromise of catalytic activity.

2. Experimental section

2.1 Materials and methods

All materials are commercially available and were used without further purification except for 5,5',5''-(methylsilanetriyl)triisophthalic acid (H_6L), which was synthesized in our laboratory.



Scheme 1 The synthesis of 5,5',5''-(methylsilanetriyl)triisophthalic acid.

2.2 Synthesis of compound 1

First, a mixture of $Ni(NO_3)_2\cdot 6H_2O$ (29 mg, 0.1 mmol) and H_6L(27 mg, 0.05 mmol) were dissolved in 6 mL of a mixed solvent (DMA:H_2O = 1:5 (V/V)), and were transferred into a 20 mL tube, which was sealed with a rubber septum and placed in a screw-capped vial. Then the resulting mixture was kept in an oven at 150 °C for 3 days under autogenous pressure. After cooled to room temperature, green block crystals were separated by centrifugation. After washing several times with DMA, the crystals were dried at ambient temperature. Yield: 36 mg (~40% based on Ni^{2+} ions). Elemental analysis (%) Calcd for compound **1**: C, 38.54; H, 3.68; N, 1.55; Found: C, 38.28; H, 3.86; N, 1.33. IR (KBr, cm^{-1}, Figure S5): 3360 (vs), 1604 (s), 1539 (s), 1401 (s), 1345 (vs), 1259 (w), 1193(w), 1121 (w), 1019 (w), 880 (w), 838 (w), 778 (w), 728 (w).

2.3 Single-crystal X-ray crystallography

Single-crystal X-ray diffraction (SXRD) data of the title compound were collected on a Bruker diffractometer using Cu Ka radiation (λ = 1.54178 Å) at 293 K. Data processing was accomplished with the SAINT processing program [26]. The structure was solved by the direct methods and refined by full-matrix least-squares fitting on F^2 using the SHELXTL crystallographic software package [27]. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. All hydrogen atoms of the organic molecule were placed by geometrical considerations and were added to the structure factor calculation. The guest molecules were disordered and could not be modelled properly, the diffused electron densities resulting from them were removed by the SQUEEZE routine in PLATONS3 and the results were appended in the CIF file. The reported refinements are of the guest-free structures using the *.hkp files produced using the SQUEEZE routine.

Crystallographic data for $\{[Ni_3HL(\mu_3\text{-}OH)(H_2O)_2]\cdot 3(H_2O)\cdot DMA\}_n$ (1893964) has been deposited with Cambridge Crystallographic Data Centre. Data can be obtained free of charge upon request at www.ccdc.cam.ac.uk/data_request/cif. Crystal data and structure refinement is summarized in Table S1.

2.4 Characterization

Powder X-ray diffraction (PXRD) of compound **1** samples were carried out on a MiniFlex 600 X-ray powder diffractometer equipped with a CuKα (λ = 1.54 Å) over 2θ range of 5-50^o at room temperature. The N_2 and CO_2 adsorption measurements were performed on automatic volumetric adsorption equipment (Quantachrome Autosorb-iQ). The samples were degassed at 150 ^{o}C for 10 hours prior to adsorption. The thermal stability of the sample was evaluated using a SDT 2960 Simultaneous DSC-TGA of TA instruments under an air atmosphere; 10 mg of the sample was heated at a heating rate of 10 ^{o}C/min up to 900 ^{o}C under nitrogen flow. Elemental analyses for C, H, and N were performed by a VarioEL analyzer. The infrared (IR) spectra (diamond) were obtained using a Nicolet 7600 FT-IR spectrometer within the 4000-500 cm^{-1} region. ^{1}H NMR spectra were recorded in $CDCl_3$ solvent on a Bruker 400 MHz spectrometer. The chemical shift is given in dimensionless δ values and is referenced relative to TMS in ^{1}H spectroscopy. Inductively coupled plasma (ICP) analyses were carried out on a Perkin-Elmer Optima 3300DV spectrometer.

For the ICP procedure, firstly, the filter liquor after catalytic reaction is incinerated at about 500 degrees in the ceramic crucible; secondly, the alkali is dissolved; thirdly, the acid is neutralized; finally, the solution is added to the instrument for analysis.

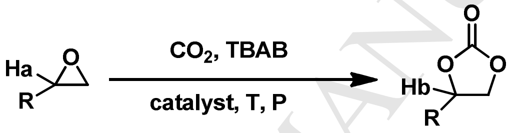
2.5 Cycloaddition of CO_2 to epoxides

Prior to gas adsorption and catalytic experiments, the crystals were immersed in methanol, and then decanted and replenished 3 times for 3 days to remove the non-volatile DMA solvates. The resulting methanol-exchanged samples of compound **1** were transferred as suspension to a Buchner funnel, and the solvents were decanted. Then the samples were degassed under a dynamic vacuum at150 °C for 10 hours. The activated materials were stored in a desiccator under vacuum.

In a typical catalytic reaction, the epoxides (20 mmol, 1850 mg for epichlorohydrin, 2400 mg for styrene oxide, 1420 mg for glycidol), activated compound **1** (0.005 mmol, 4 mg), and co-catalyst of tetrabutylammonium bromide (TBAB, 0.3 mmol) were mixed in a 20 mL autoclave reactor under solvent free environment. The reaction was purged with 1 MPa CO_2 under a constant pressure for 5 min to allow the system to equilibrate. The vessel was connected to a CO_2 source via a one-way to keep the pressure at the constant level. After that, the reactor was placed in an oil bath, and the temperature was increased to 373 K with frequent stirring under the pressurized conditions for a period of 3-12h. When the reaction was finished, the reactor was placed in an ice bath to be quickly cooled down. At the same time, the pressure was released slowly. A small aliquot of the supernatant reaction mixtures were dissolved in 0.6 mL of $CDCl_3$. The obtained solution was filtered by a syringe filter (PTFE) to be analyzed by ^{1}H NMR for calculating the conversion of the epoxide.

For the recycle experiment, the catalyst was separated by centrifugation after the reaction, and the supernatant was collected and analyzed by ^{1}H NMR. The residual solid was washed with dichloromethane and centrifuged three times and dried at 100 ◦C for 2 h under vacuum. The recovered catalyst was reused in the following reactions under the same conditions as the first run.

The conversion was calculated from ^{1}H NMR according to the following equation.



$$\text{conversion} = \frac{^1\text{Hb}}{(^1\text{Ha} + {}^1\text{Hb})}$$

The TON (turnover number) and TOF (turnover frequency) were calculated according to the following equations.

$$\text{TON} = \frac{n(\text{epoxide})}{n(\text{catalyst})}$$

$$\text{TOF} = \frac{n(\text{epoxide})}{n(\text{catalyst}) \times \text{h}}$$

3. Results and discussion

3.1 Structure characterization

Single crystal X-ray diffraction analysis revealed that compound **1** was crystalized in the space group monoclinic *C*2/c. Its formula was determined to be $\{[Ni_3HL(\mu_3\text{-}OH)(H_2O)_2]\cdot 3(H_2O)\cdot DMA\}_n$ by single-crystal X-ray diffraction, charge balance consideration, thermogravimetric analysis (TGA) and elemental analysis. The asymmetric unit of the host framework contains three crystallographically independent Ni^{2+} ions, one μ_3-OH^-, one HL^{5-} ligand and two coordinated water molecules. Ni1, Ni2 and Ni3 are bridged by six carboxyl groups into a trinuclear unit as secondary building unit (SBU), which is constructed from two [NiO_6] octahedron and one [NiO_4] tetrahedron fused at one shared OH^- corner (Fig. S1a). The trinuclear clusters are further linked by carboxylate groups to afford a porous 3D framework (Fig. 1a). Each ligand links ten Ni atoms with six carboxylate arms by four μ_2-η^1,η^1, one μ_1-η^1,η^0 and one μ_1-η^1,η^1 carboxylate groups. For clarity, the {Ni_3} cluster as a six-coordinated node is here simplified as a wine-red octahedron; while the six-connected ligand is shown as an outstretched linker with three green triangles (Fig. 1b). The assembly of abstracted geometric shape is presented in Fig. 1b. According to topological analysis, it is a 6-coordinated uninodal net with a point symbol of $\{4^{11}\cdot6^4\}$ (Fig. S2) [28]. There are four types of channels (Fig. S3), the apertures of which are about 7.9× 8.1 Å^2, 8.1 × 6.2 Å^2 and 7.8 × 3.9 Å^2 and 7.3 × 7.3 Å^2 along the *b*-axis (atom to atom distance). The solvent-accessible volume is approximately 3264 Å^3 per unit cell volume of 7875.6 Å^3, with a pore volume ratio of 41.5% calculated by the PLATON program [29]. The porosity of compound **1** was confirmed by N_2 adsorption-desorption measurements at 77K, and the result isotherm featuring type I yielded a Brunauer-Emmett-Teller (BET) surface area of 743.5 $m^2\ g^{-1}$.

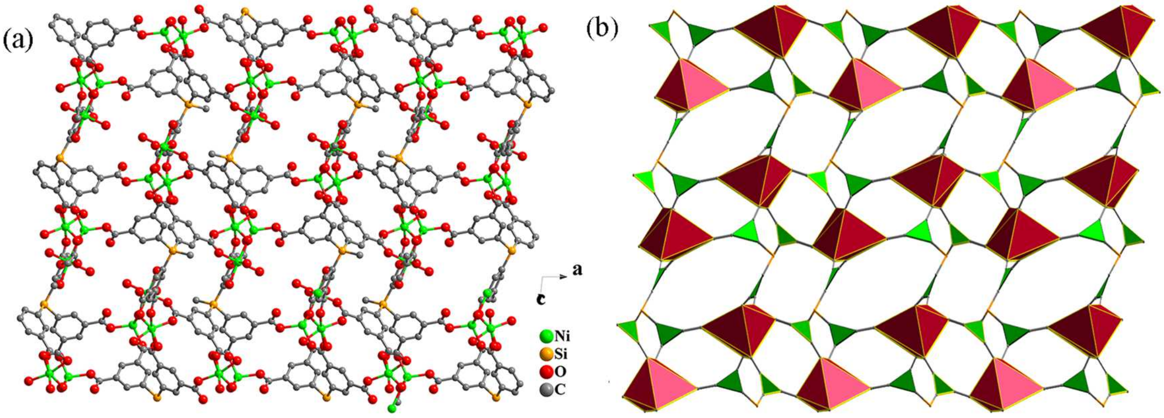


Fig.1. A view of the 3D architecture of the framework **1** in ball-stick model (a) , and the assembly of abstracted geometric shapes (b), wherein the {Ni_3} clusters are shown as octahedron, and the benzene rings are simplified as triangles.

3.2 Thermogravimetric analysis (TGA) and powder X-ray diffraction analysis (PXRD)

The thermal stability of the compound was evaluated by thermogravimetric analysis (TGA) under N_2 atmosphere. The TGA curve revealed that a weight loss of 19.53% can be observed from room temperature (RT) to 305 °C, corresponding to the loss of free water and DMA molecules, as well as the coordinated water molecules (calcd: 19.61%). With the temperature increasing, compound **1** starts to decompose.

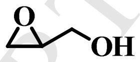
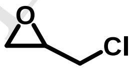
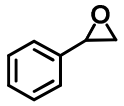
The bulk phase of compound **1** was confirmed by powder X-ray diffraction (PXRD) analyses. The diffraction patterns of fresh samples are in good agreement with the simulated ones, indicating that compound **1** is pure phase. Besides, the activated and catalyzed samples of **1** were also showed diffraction patterns similar to that of the pristine sample (Fig. S4), indicating structural permanent microporosity and integrity.

3.3 Catalytic properties

It is well known that Lewis acid sites are able to catalyze the cycloaddition of CO_2 and epoxides to produce cyclic carbonates. Therefore, polynuclear metal sites, good thermal stability and permanent porosity of **1** inspired us to explore its utilization as heterogeneous catalyst for the synthesis of cyclic carbonates by the coordinatively unsaturated Ni^{2+} ions as Lewis acidic sites. The affinity toward CO_2 for compound **1** was firstly evaluated by CO_2 sorption measurement (Fig. S8), which showed that the CO_2 uptake was up to 34.6 cm^3 g^{-1} at 273K and 1.0 atm.

The initial research was focused on the reaction of glycidol with CO_2 in the presence of n-Bu_4NBr (TBAB, 1.5 mol%) as co-catalyst under an optimum condition of 100 ^oC and 1 MPa, which is based on previous report for reference [30]. The typical reaction was performed using 20 mmol of epoxides and 0.005 mmol of compound **1**, the load of catalyst was 0.025 mol% ration based on $\{Ni_3\}$ cluster. It was found that corresponding cyclic carbonates were yielded in an approximate quantitation within 3 hours, with turnover frequency (TOF) value of ~1333 h^{-1} per $\{Ni_3\}$ cluster. Such an encouraging result inspired us to investigate other epoxides. When epichlorohydrin was employed, the reaction yield catalyzed by **1** was 95% for 3 hours, and >99% for 6 hours. A small activity decrease may be associated with different electron-withdrawing substituents [31]. During the ring opening of the epoxide, electron-withdrawing substituents facilitate nucleophilic attack [31]. The electronegativity of oxygen is bigger than chlorine, as a consequence, the yield reduced a little when hydroxyl group in glycidol was substituted by chlorine group. Above catalytic results indicate that compound **1** possesses excellent catalytic performances for small-sized epoxide substrate. To verify the catalytic generality of compound **1**, a larger epoxide substrate of styrene oxide (SO) was introduced. A significant change in the conversions were observed, and the yields of corresponding cyclic carbonate were ~39% in 3h, ~65%in 6h, and ~90% in 12 h under the same reaction conditions. This phenomenon may be mainly attributed to size effect, because the number of substrate molecule per unit porosity volume would reduce as the its size increase. However, the catalytic efficiency of compound **1** in any case is still more higher than most documented MOFs in the cycloaddition of CO_2 to epoxides, as shown in Table 1.

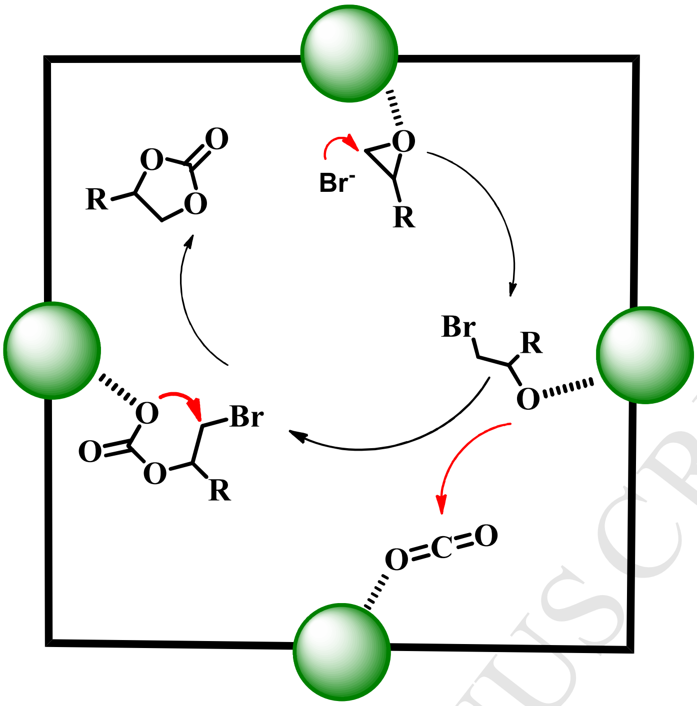
Table 1. Comparisons with the best MOF catalysts documented in the cycloaddition reaction of CO_2 and epoxides.

Catalyst	Substrate	TON	t (h)	TOF (h^{-1})	Ref.
{Eu(BTB)(phen)} [b]		20	12	2	32
1		4000	3	1333	This work
Gea-MOF-1[a]		593	6	99	33
1		4000	6	667	This work
Ni-TCPE-1[c]		2000	12	167	30
1		3600	12	300	This work

The results in this work were obtained at 373 k and under 1 MPa CO_2 pressure. Reaction conditions in other works: a, 393 K, 2.0 MPa; b, 303 K, 0.1 MPa; c, 373K, 1 MPa. TON: turnover number. The conversions were determined by ^1H NMR analysis.

Besides, reusable experiments were carried out to verify the heterogeneous nature of compound **1**. Herein, the glycidol was employed as the substrate in view of high conversion and easy segregation of its cycloaddition. Since a complete conversion for glycidol took 3 hours, the catalyst was isolated and reused every 3 hours, and the conversions were determined by ^{1}H NMR analysis. It was found that the yields did not obviously decrease even after five successive runs (Fig. S9). In addition, it is worth noting that the loading is very small. An unavoidable loss of catalyst would cause an inaccurate decrease of yield. After the fifth reaction, inductively coupled plasma (ICP) analysis was performed on the mixture filtrate. There was no Ni leaching, further proving that the reaction catalyzed by compound **1** was indeed heterogeneous. Besides, PXRD measurements were used to confirm the structural integrity of the recovered catalyst (Fig. S4).

A reasonable mechanism was proposed for the cyclic addition of CO_2 and epoxides in the presence of compound **1** (Scheme 2), similar to that of previous reports [30, 33]. After pretreatment at 150 ^{o}C, the coordinated H_2O molecules were removed to form unsaturated coordinative Ni atoms, then the $\{Ni_3\}$ clusters could act as Lewis acid. Firstly, the CO_2 and substrate molecules enter channels and are adsorbed on the Lewis acid sites of activated **1**, and the unsaturated coordinative Ni synchronously binds to the oxygen atom of epoxide, making it more susceptible for ring-opening. Secondly, the nucleophilic reagent Br^- of TBAB attacks the activated carbon atom of epoxide, leading to the ring open and producing the metal/heteroatom alkoxide intermediates (step 1). Finally, the anion intermediate reacts with CO_2, and the ring-closure forms the final cyclic carbonate. At the same time, the Br^- and the catalyst are regenerated, respectively.



Scheme 2 The proposed mechanism of the cyclic addition of CO_2 and epoxide catalyzed by activated **1** (dark rectangle: channel; green sphere: {Ni_3} cluster).

4. Conclusions

In summary, a new and highly efficient catalyst based on {Ni_3} cluster has been developed. The compound catalyzes the coupling reaction of epoxides with CO_2 at 373K and under 1 MPa CO_2 pressure to produce cyclic carbonates with high yields. Intensive investigation including cycle experiments and catalyst filtration test confirm that activated **1** operates as a heterogeneous catalyst. Moreover, its catalytic activity remains high after several reuses.

Acknowledgments. This work was financially supported by the Doctoral Scientific Research Foundation of Inner Mongolia University for Nationalities (BS462), the Open Projects Founded by Inner Mongolia Key Lab of Carbon Nanomaterials (MDK2018040), the Open Projects Founded by Inner Mongolia Key Laboratory for the Natural Products Chemistry and Functional Molecular Synthesis (MDK2017053, MDK2017056), and the Scientific Research Program of Inner Mongolia University for Nationalities (NMDGP1703 and NMDYB1728).

References

[1] Q. Wang, J. Luo, Z. Zhong, A. Borgna, Energy Environ. Sci. 4 (2011) 42–55.

[2] J. Ma, N. Sun, X. Zhang, N. Zhao, F. Xiao, W. Wei, Y. Sun, Catal. Today 148 (2009) 221–231.

[3] I. Omae, Coord. Chem. Rev., 256 (2012) 1384–1405.

[4] M. North, R. Pasquale and C. Young, Green Chem., 12 (2010) 1514–1539.

[5] Y. N. Li, R. Ma, L. N. He and Z.-F. Diao, Catal. Sci. Technol., 4 (2014) 1498–1512.

[6] B. Yu and L. N. He, ChemSusChem, 8 (2015) 52–62.

[7] M. Ding and H.-L. Jiang, ACS Catal., 8 (2018) 3194-3201.

[8] M. Ding, S. Chen, X.-Q. Liu, L.-B. Sun, J. Lu and H.-L. Jiang, ChemSusChem, 10 (2017) 1898-1903.

[9] W. Jiang, J. Yang, Y.-Y. Liu, S.-Y. Song and J.-F. Ma, Chem. Eur. J., 22 (2016) 16991-16997.

[10] B. Schäffner, F. Schäffner, S.P. Verevkin, A. Börner, Chem. Rev. 110 (2010) 4554.

[11] B. Chatelet, L. Joucla, J. P. Dutasta, A. Martinez, K. C. Szeto and V. Dufaud, J. Am. Chem. Soc., 135 (2013) 5348-5351.

[12] B. H. Xu, J. Q. Wang, J. Sun, Y. Huang, J. P. Zhang, X. P. Zhang and S. J. Zhang, Green Chem., 17 (2015) 108-122.

[13] X.-B. Lu and D. J. Darensbourg, Chem. Soc. Rev., 41 (2012) 1462-1484.

[14] M.-P. Liu, Y.-P. Luo, L. Xu, L. Sun and H.-B. Du, Dalton Trans., 45 (2016) 2369-2373.

[15] M. E. Wilhelm, M. H. Anthofer, M. Cokoja, I. I. E. Markovits,W. A. Herrmann and F. E. Kuhn, ChemSusChem, 7 (2014) 1357-1360.

[16] Q. Sun, N. Wang, Q. Bing, R. Si, J. Liu, R. Bai, P. Zhang, M. Jia, and J. Yu, Chem, 3 (2017) 477-493.

[17] M. North, R. Pasquale and C. Young, Green Chem., 12 [2010] 1514-1539.

[18] H.-C. Zhou, J. R. Long and O. M. Yaghi, Chem. Rev., 112 (2012) 673-674.

[19] M. Ding and H.-L. Jiang, ACS Catal., 8 (2018) 3194-3201.

[20] J. Zhao, W.-W. Dong, Y.-P. Wu, Y.-N.Wang, C. Wang, D.-S. Li and Q.-C. Zhang, Mater. Chem. A, 3 (2015) 6962-6969.

[21] (a) W.-W. Xiong, J. Miao, K. Ye, Y. Wang, B. Liu, Q. Zhang, Angew Chem Int. Ed., 54 (2015) 546-550; (b) W.-W. Xiong, Q. Chun, Angew Chem. Int. Ed., 54 (2015) 11616-11623; (c) P. Li, F.-F. Cheng, W.-W. Xiong, and Q. Chun, Inorg. Chem. Front., 1 (2014) 292-301; (d) W.-W. Xiong, E. U. Athresh, Y. T. Ng, J. Ding, T. Wu, and Q. Chun, J. Am. Chem. Soc., 135 (2013) 1256-1259; (e) W.-W. Xiong, P.-Z. Li, T.-H. Zhou, A. L. Y. Tok, R. Xu, Y. Zhao, and Q. Zhang, Inorg. Chem., , 52 (2013) 4148-4150; (f) D.-D., Yang, Y. Song, B. Zhang, N.-N. Shen, G.-L. Xu, W.-W. Xiong, and X.-Y. Huang, Cryst. Growth Des., 18 (2018) 3255−3262; (g) W.-W. Xiong, G. Zhang, and Q. Zhang, Inorg. Chem. Front. , 5 (2018) 2693-2708.

[22] H.-X. Zhang, M. Liu, T. Wen and J. Zhang, Coord. Chem. Rev., 307 (2016) 255-266.

[23] K. J. Lee, J. H. Lee, S. Jeoung and H. R. Moon, Acc. Chem. Res., 50 (2017) 2684-2692.

[24] T. Zhang and W. Lin, Chem. Soc. Rev., 43 (2014) 5982-5993.

[25] M. H. Beyzavi, C. J. Stephenson, Y. Liu, O. Karagiaridi, J. T. Hupp and O. K. Farha, Front. in Energy Res., 2 (2015) 63.

[26] SMART and SAINT software package, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1996.

[27] (a) O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Cryst. 42 (2009) 339-341; (b) G. M. Sheldrick, ActaCryst. A, 64 (2008) 112-122; (c) G. M. Sheldrick, ActaCryst. C, 71 (2015) 3-8.

[28] V. A. Blatov, Struct. Chem., 23 (2012) 955-963, TOPOS software is available for download at http://www.topos.samsu.ru.

[29] A. L. Spek, J. Appl. Crystallogr., 36 (2003) 7-13.

[30] Z. Zhou, C. He, J. Xiu, L. Yang and C. Duan, J. Am. Chem. Soc. 137 (2015) 15066.

[31] A. Kilic, A. A. Palali, M. Durgun, Z. Tasci, M. Ulusoy, Spectrochim. Acta Part A. 113 (2013) 432-438.

[32] H. Xu, B. Zhai, C.-S. Cao, and B. Zhao, Inorg. Chem., 55 (2016) 9671-9676.

[33] V. Guillerm, Ł. J. Weseliński, Y. Belmabkhout, A. J. Cairns, V. D'Elia, Ł. Wojtas, K. Adil and M. Eddaoudi, Nature Chem. 6 (2014) 673-680.

► A {Ni_3}-cluster based network has been successfully developed as an efficient catalyst for CO_2 cycloaddition.

► Its catalytic activity is superior to most documented MOF-based catalysts.

► The heterogeneous catalyst can be recycled at least five runs without a significant compromise of catalytic activity.