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CO_2 conversion: the potential of porous-organic polymers (POPs) for catalytic CO_2–epoxide insertion†

Mohamed H. Alkordi,‡§[a] Łukasz J. Weseliński,‡¶[a] Valerio D'Elia,‖[b] Samir Barman,[b] Amandine Cadiau,[a] Mohamed N. Hedhili,[c] Amy J. Cairns,[a] Rasha G. AbdulHalim,[a] Jean-Marie Basset[b] and Mohamed Eddaoudi*[a]

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Novel porous organic polymers (POPs) have been synthesized using functionalized Cr and Co–salen complexes as molecular building blocks. The integration of metalosalen catalysts into the porous polymer backbone permits the successful utilization of the resultant functionalized material as a solid-state catalyst for CO_2–epoxide cycloaddition reactions with excellent catalytic performance under mild conditions of temperature and pressure. The catalysts proved to be fully recyclable and robust, thus showing the potential of POPs as smart functional materials for the heterogenization of key catalytic elements.

1. Introduction

CO_2 reutilization is regarded as a plausible strategy to mitigate the waste CO_2 emissions from energy intensive industrial and human activities.[1] Therefore, the deployment of advanced technologies aiming to exploit CO_2 as a feedstock for the synthesis of valuable chemical products is highly desirable.[2] In this context, the synthesis of industrially relevant[3] cyclic organic carbonates from CO_2 and epoxides is gaining interest as a process that can be implemented under relatively mild conditions using recently developed homogeneous catalysts.[4,5] Nevertheless, the immobilization of such catalytic moieties to yield recoverable and reusable catalysts with preserved activity and selectivity remains an ongoing challenge.

Towards this goal, novel porous materials with adequate pore volume and surface area, strong affinity to CO_2, and appropriate stability are being sought as prospective candidates to tackle this challenge. Porous-Organic Polymers (POPs) represent a promising class of sorbents that can fulfill the abovementioned criteria.[6] Interestingly, the ability to assemble POPs using the molecular building block (MBB) approach offers potential to fine-tune their chemical composition and the resultant pore size, shape and functionality to address a given targeted application. Markedly, the predominant covalent character of these materials offers high thermal and chemical stability that permits the potential utilization of POPs under practical reaction conditions. Rationally, the potential POPs were recognized for applications pertaining to gas storage and separation,[6g,7] photoelectronics[8] and catalysis.[9]

Salen complexes are widely recognized in catalysis[10] and proven to be effective homogeneous catalysts for the cycloaddition of CO_2 to epoxides.[11] Interest in heterogeneous metal-osalen-based catalysts is largely driven by the quest to alleviate two major limitations commonly encountered in homogeneous catalysis, namely difficult separation/recovery of the catalyst from the reaction mixture and the limited catalyst lifetime due to either bimolecular deactivation leading to bridged μ-oxide dimers[10b] (hindered access to catalytic sites) and/or oxidative self-degradation. Therefore, the immobilization of metal-osalens on solid matrices provides a promising approach to isolate and protect the catalytic sites of the metallacycle, and subsequently overcome the aforementioned drawbacks.

A few examples on the application of metalosalen-POPs as heterogeneous catalysts for the title cycloaddition have been

[a]Functional Materials Design, Discovery and Development Research Group (FMD[3]), Advanced Membranes and Porous Materials Center (AMPMC), Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Kingdom of Saudi Arabia. E-mail: mohamed.eddaoudi@kaust.edu.sa

[b]KAUST Catalysis Center (KCC), King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Kingdom of Saudi Arabia

[c]Imaging and Characterization Laboratory, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Kingdom of Saudi Arabia

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‡ These authors contributed equally to this work.

§ Current address: Zewail City of Science and Technology, Center for Materials Science, Sheikh Zayed Dist., 6th of October, 12588, Giza, Egypt.

¶ Current address: Department of Chemistry, Michigan Technological University, 1400 Townsend Drive, Houghton, Michigan 49931, USA.

‖ Current address: Department of Materials Science and Engineering, Vidyasirimedhi Institute of Science and Technology, 21210, WangChan, Rayong, Thailand.

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recently reported.[12] However, only few compounds have been investigated in spite of a large variety of metalosalens conceivable, depending on the choice of the metal, organic backbone and counter-ion. Here, we report the application of novel metalosalen-containing POPs as heterogeneous catalysts for the synthesis of cyclic carbonates from epoxides and CO_2. The reported catalysts showed remarkable catalytic activities, under relatively mild reaction conditions, and excellent recyclability properties, *i.e.* convenient separation and multiple reuse of the material.

2. Experimental

Materials and methods

All reagents were commercially available and used as received unless further noted. NMR spectra were recorded at room temperature with a Bruker Avance III 500 MHz spectrometer using $CDCl_3$ as a solvent. Cross polarization magic angle spinning (CP-MAS) solid state ^{13}C NMR spectra were recorded with a Bruker Avance 600 WB spectrometer. Elemental analysis was performed with a Thermo Scientific Flash 2000 instrument. Powder X-ray diffraction (PXRD) measurements were carried out at room temperature on a PANalytical X'Pert PRO diffractometer 45 kV, 40 mA for CuKα ($\lambda = 1.5418$ Å) with a scan speed of 0.02° min^{-1} and a step size of 0.008° in 2θ. UV spectra were recorded with a Perkin Elmer Lambda 950 UV/VIS spectrometer. Thermogravimetric analysis (TGA) measurements were performed on a TA Q500 apparatus, under air atmosphere (flow = 25 cm^3 min^{-1}, heating rate 5 °C min^{-1}). Fourier-transform infrared (FT-IR) spectra (4000–600 cm^{-1}) were recorded on a Thermo Scientific Nicolet 6700 apparatus. Low-pressure gas adsorption measurements were performed on a fully automated Autosorb 6B (for N_2 sorption screening) and an Autosorb-iQ gas adsorption analyzer (Quantachrome Instruments) at pressures up to 1 atm. The cryogenic temperatures 77 K and 87 K were attained using liquid nitrogen and argon baths, respectively. Pore size distributions were calculated using a QSDFT pore size analysis method for carbons with slit-shaped/cylindrical/spherical pores. ICP-OES measurements of the metal loading on a porous material were carried out on a Varian 720-ES instrument after digestion of a 10 mg sample in *aqua regia*. XPS studies were carried out on a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al Kα X-ray source ($h\nu$ = 1486.6 eV) operating at 150 W, a multichannel plate and a delay line detector under a vacuum of 1–10^{-9} mbar. The survey and high-resolution spectra were collected at fixed analyzer pass energies of 160 eV and 20 eV, respectively. Samples were mounted in a floating mode in order to avoid differential charging. Charge neutralization was required for all samples. Binding energies were referenced to the aromatic sp^2 hybridized (C=C) carbon for the C 1s peak set at 284.5 eV. The morphology of samples was determined by using a field-emission scanning electron microscope (FESEM, FEI Nova Nano 630). The chemical compositions of samples were analyzed by using an energy dispersive spectrometer (EDX, Quanta 600).

Synthesis of *N*,*N*′-bis(5-bromosalicylaldehyde)cyclohexanediimine

The compound was prepared following a reported procedure.[13] A suspension of *trans*-cyclohexane-1,2-diamine (1.71 g, 15 mmol) and 5-bromo-2-hydroxybenzaldehyde (6.03 g, 30 mmol) in absolute ethanol (20 ml) was vigorously stirred at 75 °C under Ar for 14 h. It was cooled, filtered on paper, washed thoroughly with ethanol and dried on air to produce a yellow solid, 6.56 g (97%). ^1H NMR (500 MHz, $CDCl_3$) δ = 13.3 (s, 2H), 8.18 (s, 2H), 7.33 (dd, J = 2.4, 8.8 Hz, 2H), 7.26 (s, 2H), 6.80 (d, J = 8.8 Hz, 2H), 3.33 (m, 2H), 1.90 (m, 4H), 1.74 (m, 2H), and 1.47 (m, J = 9.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 163.6, 160.1, 135.1, 133.7, 120.0, 119.0, 110.3, 72.8, 33.0, and 24.2.

Synthesis of 1

The material was synthesized following the reported procedure.[14] In a 150 ml oven-dried round bottom flask, a solution of *N*,*N*′-bis(5-bromosalicylaldehyde)cyclohexanediimine (0.96 g, 2 mmol) in dry DMF (30 ml, stored over CaH_2) and dry triethylamine (6 ml) was bubbled with Ar for 30 min. Then, 1,3,5-triethynylbenzene (0.3 g, 2 mmol), $PdCl_2(PPh_3)_2$ (44 mg, 0.063 mmol), and CuI (12 mg, 0.063 mmol) were added in one portion, the flask was evacuated/backfilled with Ar three times, sealed with septum and heated at 80 °C for 50 h with vigorous stirring. It was cooled, filtered, solid washed sequentially with DMF, water, THF, MeOH and acetone, then suspended in 1 : 1 THF/CH_2Cl_2 (80 ml), and stirred at rt for 48 h, refreshing solution twice daily. It was filtered, washed with THF and dried at high vacuum at 60 °C overnight to give red-brown solid, 0.57 g. Calc. for $C_{33}H_{26}N_2O_2$: C, 82.13%; H, 5.43%; N, 5.81%; O, 6.63%. Found C, 79.8%; H, 4.58%; N, 4.16%. The proposed elemental composition is based on a 1 : 1 reaction between the salen moiety and the polytopic 1,3,5-triethynylbenzene linker. As suggested in other studies,[14] factors such as chain termination by halogen atoms and residual halogen impurities, variable chain length, incomplete metalation and, possibly, homocoupling between the polytopic linker units can lead to a discrepancy between the elemental analysis values and those expected based on the stoichiometry of copolymerization. This is observed in this case and also for **1-Co** and **1-Cr**. In particular, this may result in a significant relative deviation with regards to the proposed N content as it is present in small proportions relative to C. Nevertheless, the ICP, EDX and XPS analyses (*vide infra*) confirmed the expected metal content and the expected N/metal ratio.

Synthesis of 1-Co

In a 150 ml oven-dried round bottom flask, a solution of *N*,*N*′-bis(5-bromosalicylaldehyde)cyclohexanediimine (0.96 g, 2 mmol) and $CoBr_2$ (0.438 g, 2 mmol) in dry DMF (30 ml, stored over CaH_2) was heated at 110 °C under Ar for 30 min. It was cooled to afford a deep green solution. To the solution of the metallated salen ligand, dry triethylamine (6 ml) was added causing a change of color to deep red. The flask was evacuated/backfilled with Ar twice, and the mixture bubbled with Ar for

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30 min. Then, 1,3,5-triethynylbenzene (0.3 g, 2 mmol), $PdCl_2(PPh_3)_2$ (44 mg, 0.063 mmol), and CuI (12 mg, 0.063 mmol) were added in one portion, the flask was evacuated/backfilled with Ar three times, sealed with septum and heated at 80 °C for 48 h with vigorous stirring. It was cooled, filtered and the solid was washed sequentially with DMF, water, THF, MeOH and acetone, then suspended in 1 : 1 : 1 : 1 CH_2Cl_2/H_2O/MeOH/acetone (160 ml), and stirred at 80 °C for 20 h under air. It was filtered, washed with acetone and dried at high vacuum at 60 °C overnight to produce dark red solid, 1.35 g. Calc. for $C_{33}H_{24}N_2O_2$-CoBr: C, 63.99%; H, 3.91%; Br, 12.9%; Co, 9.51%; N, 4.52%; O, 5.17%. Found C, 55.58%; H, 3.48%; N, 4.00%.

Synthesis of 1-Cr

In a 150 ml oven-dried round bottom flask, a solution of *N*,*N*′-bis(5-bromosalicylaldehyde)cyclohexanediimine (0.96 g, 2 mmol) and $CrCl_2$ (0.246 g, 2 mmol) in dry DMF (30 ml, stored over CaH_2) was heated at 110 °C under Ar for 30 min. It was cooled to afford dark brown solution. To the solution of the metallated salen ligand, dry triethylamine (6 ml) was added, the flask was evacuated/backfilled with Ar twice, and the mixture was bubbled with Ar for 30 min. Then, 1,3,5-triethynylbenzene (0.3 g, 2 mmol), $PdCl_2(PPh_3)_2$ (44 mg, 0.063 mmol), and CuI (12 mg, 0.063 mmol) were added in one portion and the same synthetic procedure and work-up as for **1-Co** was followed to give green brown solid, 0.6 g. Calc. for $C_{33}H_{24}N_2O_2CrCl$: C, 69.78%; H, 4.26%; Cl, 6.24%; Cr, 9.15%; N, 4.93%; O, 5.63%. Found C, 68.16%; H, 3.90%; N, 2.44%.

Catalysis studies

In a typical setup **1-Cr** (50 mg, 0.1 mmol of Cr, 0.2 mol%), NBu_4Br (73.2 mg, 0.2 mmol, 0.4 mol%) and propylene oxide (PO) (3.5 ml, 50 mmol) were charged in a 100 ml stainless steel autoclave and CO_2 was added to the system until an internal pressure of 16 bar was reached. The reactor was heated up to 100 °C, with the internal pressure stabilized at 20 bar (initial pressure). The mixture was stirred for 16 hours. After this period the system was allowed to cool to room temperature. The reaction vessel was cooled down with ice and the pressure was slowly released. The crude mixture was analyzed by NMR to determine propylene oxide conversion by comparison between the integrals of the corresponding protons of the starting epoxide and the carbonate product as in ref. 4*a*. The catalyst was recovered by decanting the liquid phase and subsequently suspended in dichloromethane. Dichloromethane was decanted and the catalyst was washed again with fresh dichloromethane. Decantation of the solvent afforded a solid that was dried in an oven at 80 °C for 8 hours. The amount of catalyst recovered for each cycle corresponded to 94–96% of the initial amount.

3. Results and discussion

We utilized the Sonogashira–Hagihara cross-coupling reaction to construct POPs through linkage of the tailored ditopic salen molecules containing two bromophenyl groups and the tritopic linker 1,3,5-triethynylbenzene (Scheme 1). The cross-coupling reaction of the non-metalated dibromosalen with 1,3,5-triethynylbenzene resulted in an amorphous, porous solid (**1**). The metalated salen solutions (cobalt and chromium, respectively) were prepared *in situ* prior to Sonogashira coupling. The cobalt-metalated salen POP (**1-Co**) was obtained as deep-red crystalline, porous solid under similar reaction conditions. Accordingly, chromium dibromosalen afforded the chromium-metalated salen POP (**1-Cr**) as a brown porous solid.

SEM images of **1-Co** indicated smoother surface morphology as compared to the surface of **1-Cr**, further supporting the micro-crystallinity observed for **1-Co** as compared to the largely amorphous nature of **1-Cr** inferred from X-ray powder diffraction (for PXRD data, see Fig. S1, ESI†). Additionally, both polymers show uniform particle dispersity as shown in Fig. S12, ESI.† The solids were insoluble in water and common organic solvents. Thermogravimetric analysis of all three materials showed loss of weight taking place only above 300 °C, thus confirming the robustness of the compounds (Fig. S3, ESI†).

The N_2 sorption isotherms (Fig. 1 and S5, ESI†) of **1**, **1-Co**, and **1-Cr** confirmed their permanent porosity (the measured BET surface areas are 523 $m^2\ g^{-1}$ for **1**, 370 $m^2\ g^{-1}$ for **1-Co** and 732 $m^2\ g^{-1}$ for **1-Cr**). A comparison with the POPs reported by Xie *et al.*[12a] (Scheme 1) shows relatively lower surface areas of our materials. In particular, the non-metalated compounds **1** and **2** display a noticeable difference (772 $m^2\ g^{-1}$ for **2** *versus* 523 $m^2\ g^{-1}$ for **1**) that could be attributed to the steric influence of the *tert*-butyl groups in **2**.

Interestingly, notable changes in the surface area were noticed for the analogous structures metalated with Co (772 $m^2\ g^{-1}$ and 965 $m^2\ g^{-1}$ for **2** to **2-Co**, and 523 $m^2\ g^{-1}$ and 370 $m^2\ g^{-1}$ for **1** to **1-Co**), indicating significant effect of the starting metal complex on the structural properties of resulting POPs. **1-Co** is a crystalline material, as compared to amorphous **1** and **1-Cr**, see Fig. 1, ESI.† Finally, **1-Cr** and **2-Cr**, and **1-Co** and **2-Co** display surface areas comparable to the POPs prepared by Chun *et al.*[12b] (650 $m^2\ g^{-1}$ for **3-Al**, 580 $m^2\ g^{-1}$ for **3-Co** and 522 $m^2\ g^{-1}$ for **3-Cr**, Scheme 1) with the use of tetrahedral linker, tetra-(4-ethynylphenyl)methane and in the presence of *tert*-butyl groups on the salen scaffold.

This shows that the final surface area of the metalated porous solids is strongly dependent on the metal and on the pattern of substitution at the salen scaffold.

The successful salen metalation in **1-Co** and **1-Cr** is indicated by the observed solid-state UV-Vis (Fig. S4, ESI†) and FT-IR (Fig. S2, ESI†) spectra of the fully washed solids. The characteristic absorption bands for the O–H stretching (phenol, ν = 3294 cm^{-1}) was significantly reduced following metalation in both **1-Co** and **1-Cr**, indicating deprotonation of the phenolic hydroxyl groups. The UV-Vis spectra for **1-Co** and **1-Cr** exhibit typical absorption bands at λ_{max} of 486 and ~400 nm, respectively, characteristic for the metal salen complexes.[15]

ICP-OES analysis confirmed a Co loading of 8.05 wt% (calculated theoretical maximum loading is 9.51 wt%) and a Cr loading of 7.12 wt% (calculated theoretical maximum loading is 9.15 wt%). These results were further supported by EDX analysis of the polymers, see Fig. S13–S15, ESI.† The difference between

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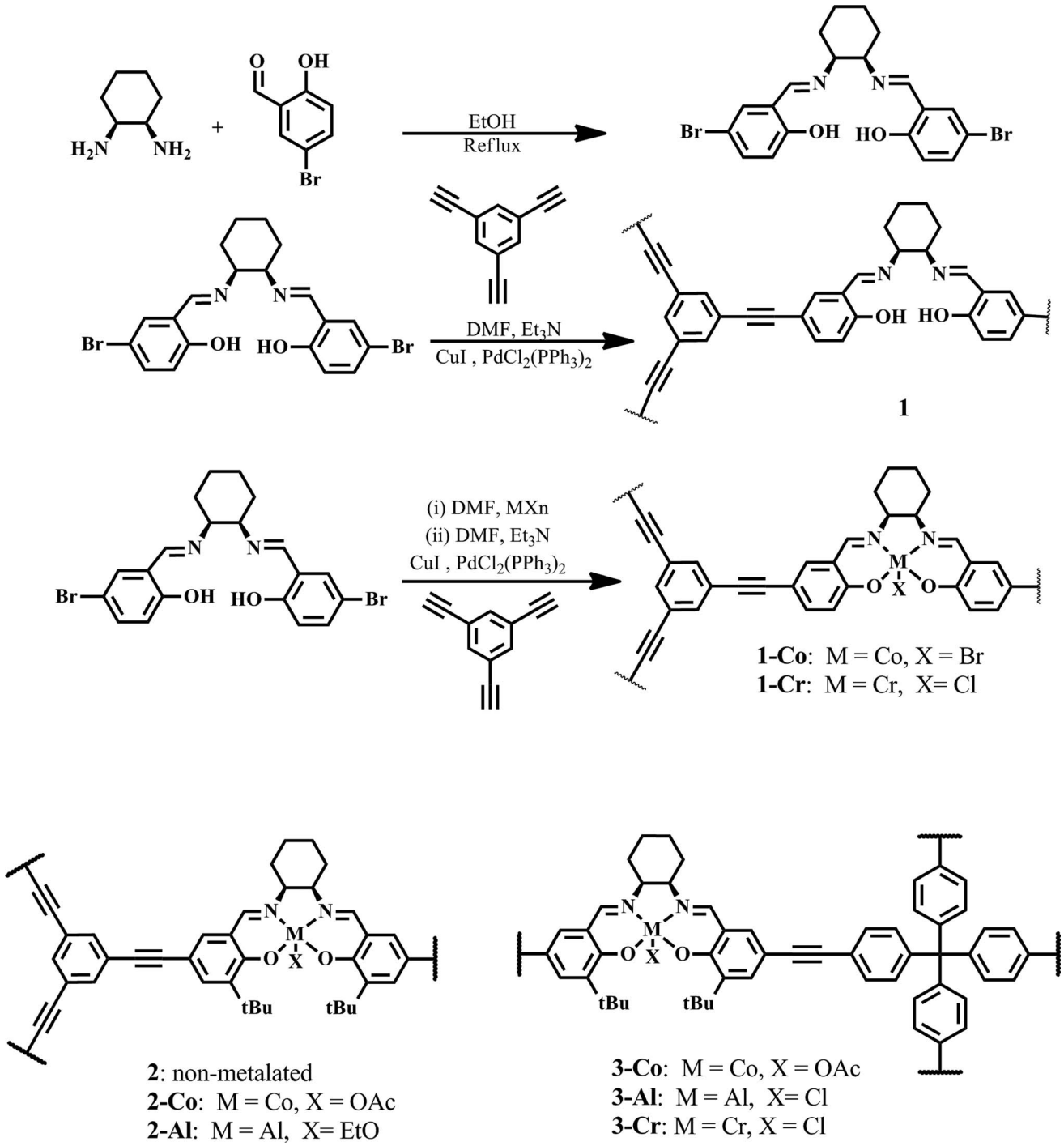

Scheme 1 Synthesis of **1**, **1-Co** and **1-Cr** and comparison with other metalosalen-based POPs (**2-Co** and **2-Al**, ref. 12*a* and **3-Co**, **3-Al** and **3-Cr**, ref. 12*b*).

the theoretical and experimental loading may be attributed to the incomplete metalation of some inaccessible salen's coordination sites at the preparation stage, or competing coordination of the metal ions by the Et_3N base used in the synthesis, and consistent with the observation of a residual OH stretching signal at 3294 cm^{-1} in the FT-IR spectra (Fig. S2, ESI†). The XPS spectra of **1-Co** and **1-Cr** display the signals relative to the $2p_{3/2}$ orbitals of the metal centers at 779.5 eV and at 576.6 eV respectively. According to the available XPS literature data for Cr[16] and Co,[17] the metals were found to be in a formal +3 oxidation state (see Fig. S7–S10, ESI,† for a more detailed explanation of the XPS spectra of both compounds). The N/metal ratio of *ca.* 2 found for **1-Cr** and **1-Co** from the XPS survey spectra in Fig. S7 and S9† respectively is in a good agreement with the proposed structures and confirms the successful metalation of the salen scaffolds.

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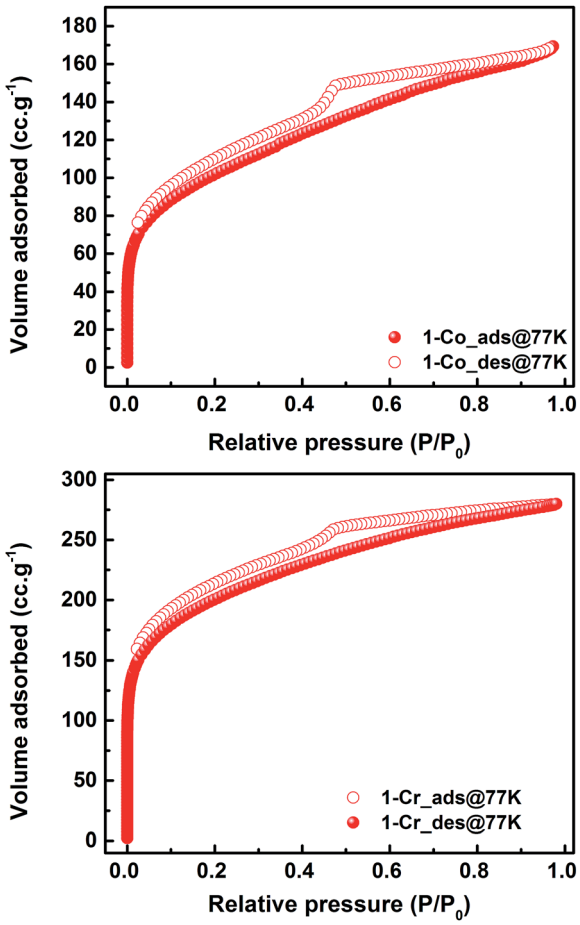

Fig. 1 N_2 sorption isotherms of **1-Co** (370 m^2 g^{-1}), and for **1-Cr** (732 m^2 g^{-1}) confirming the porous nature of the solids.

Homogenous Al–, Mn–, Cr–, Co– and Zn–salen complexes generally show high catalytic activities towards the cycloaddition of epoxides and CO_2 under mild reaction conditions.[11] Nevertheless, heterogeneous and recyclable metalosalen catalysts obtained by tethering the catalytic moieties to the traditional solid supports have proven far less active as compared to their soluble counterparts. These results are rationalized as an effect of the immobilization and limited accessibility of the catalytically active core.[18] Among the heterogeneous systems showing significant activity under mild conditions,[18b,19] MOFs[20] and porous organic polymers[12,21] have emerged as valuable catalysts for the cycloaddition of CO_2 and epoxides in virtue of the high accessibility of the catalytically active centers.

In this study, catalysts **1-Co** and **1-Cr** showed both remarkable activities towards the formation of cyclic carbonates under mild reaction conditions (see Table 1) in the presence of two equivalent amounts of tetrabutylammonium bromide (NBu_4Br) as a nucleophilic co-catalyst. Very high to nearly quantitative conversions were obtained for mono-substituted epoxides **4a–4c** (Table 1, entries 5, 7, 9 for **1-Cr**; entries 15, 17, 19 for **1-Co**) at 100 °C under 20 bar of CO_2. Epoxide **2c** proved to be the most reactive substrate for this reaction (Table 1, entries 9, 19); nearly quantitative yields of the corresponding carbonate product were obtained after 7 h even when using only half amount of the catalyst employed for epoxides **4a** and **4b**. Disubstituted epoxide **4d** (Table 1, entries 11, 21) afforded only low yields of the corresponding product of cycloaddition as an effect of the increased steric bulk. The catalysts were recovered and reused for three additional catalytic cycles for each of **4a–4c** substrates showing outstanding recyclability; the small drop in conversions observed can be mostly attributed to some catalyst loss due to handling at the recovery stage (Table 1, entries 6, 8, 10 for **1-Cr**, entries 16, 18, 20 for **1-Co**). Leaching of metal species was negligible as confirmed by ICP-OES analysis. Under the same reaction conditions, the metal-free polymer **1** showed much lower catalytic activity for the conversion of epoxide **4a** (34% compared to 98% observed using **1-Cr** and 89% observed for **1-Co** Table 1, entries 2, 5, and 15 for the reaction at 100 °C and 20 bar CO_2). This can be attributed to the catalytic activity of the free phenol groups as reported by other authors.[22] The NBu_4Br co-catalyst, used in the absence of POPs, showed residual catalytic activity both at 22 °C and at 100 °C (Table 1, entry 1) but much lower than when used in combination with **1-Co** and **1-Cr** under identical reaction conditions.

Further investigation of the activity of **1-Co** and **1-Cr** was dedicated to their catalytic performance under even milder conditions. When the reaction was performed at 75 °C, moderate to good conversions were obtained for both catalysts (Table 1, entries 4 and 14). Then, **1-Co** and **1-Cr** were tested for the reaction between **4a** and CO_2 under ambient conditions (25 °C, 1 bar CO_2). The catalysts proved to be active even under such challenging reaction conditions, although only low yields of the corresponding carbonate were obtained after 48 h (19% and 25% for **1-Cr** and for **1-Co** respectively, Table 1, entries 3 and 12). A comparison between **1-Co** and the analogous Co salen-based microporous polymer developed by Xie *et al.*[12a] (**2-Co**) and employed under comparable reaction conditions, but using up to 15 equiv. of NBu_4Br per mole of metal as a co-catalyst for 48 h, shows a slightly higher TON (167 *vs.* 125) in favor of the latter POP. In our case, increasing the NBu_4Br/Co molar ratio from 2 to 15 did not have any substantial effect on the catalytic performance (Table 1, entry 13). The difference in activity under ambient conditions, observed for **2-Co** (Scheme 1), and our materials can be explained on the basis of a combination of both electronic and structural effects. Indeed, complexes **1-Co** and **2-Co** differ for the presence of *t*-butyl substituents at the aromatic ligands and for the counter-ions of the cobalt cations (Br^- in our work, AcO^- for Xie work). It is well known that both factors can have a strong influence for tuning the catalytic activity of the salen complex metal centers, by altering its Lewis acidity.[11,23] This is known to have a strong impact on the interaction between the nucleophilic co-catalyst and the metal center, on the ability of the latter to activate the epoxide for ring opening and on the following steps of CO_2 insertion and release of the carbonate product *via* cyclization. The barrier for these steps is known to depend on a fine balance between the Lewis acidity of the metal center and the nucleophilicity and basicity of the co-catalyst.[4b,24] In this context, the presence of electron donating *t*-butyl substituents at the aromatic rings has been found to have a dramatic effect on the yield of the cycloaddition reaction of CO_2 to epoxides catalyzed

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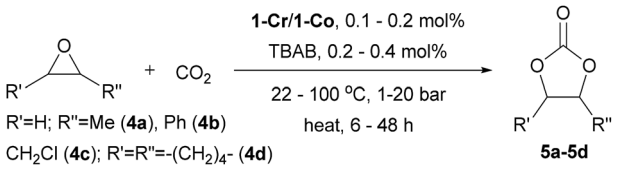
Table 1 Catalytic activity of **1-Cr** and **1-Co** for the reaction of CO_2 to epoxides **4a–4d**



Entry	R″	Time (h)	Temp. (°C)	Conversion[a] (%)	TON[b]	TOF (h^{-1})	Entry	R″	Time (h)	Temp. (°C)	Conversion[a] (%)	TON[b]	TOF (h^{-1})
(Catalyst: **1-Cr**)[c,d]							(Catalyst: **1-Co**)[i,j]						
1[e]	Me	48 (6)	22 (100)	5 (14)			12[j,g]	Me	48	22	25	125	3
2[f]	Me	48 (16)	22 (100)	8 (34)			13[k,g]	Me	48	22	26	130	3
3[c,g]	Me	48	22	19	139	3	14[j]	Me	16	75	61	223	14
4[d]	Me	16	75	68	248	15	15[j]	Me	16	100	89	325	20
5[d]	Me	16	100	98	358	22	16[j,h]	Me	16	100	88, 83, 79		
6[d,h]	Me	16	100	95, 90, 85			17[j]	Ph	6	100	97	354	59
7[d]	Ph	6	100	82	299	50	18[j,h]	Ph	6	100	85, 82, 79		
8[d,h]	Ph	6	100	75, 70, 69			19[i]	CH_2Cl	7	100	92	672	96
9[c]	CH_2Cl	7	100	95	693	99	20[i,h]	CH_2Cl	7	100	88, 82, 79		
10[c,h]	CH_2Cl	7	100	90, 87, 83			21[i]	$-(CH_2)_4-$	6	100	20	146	24
11[c]	$-(CH_2)_4-$	6	100	28	204	34							

[a] Determined by ^{1}H NMR (in $CDCl_3$) on an aliquot of the final reaction mixture by comparison of the intensities of signals relative to the corresponding protons for the starting material and the product. [b] mmol of product/mmol of Cr or Co employed. [c] Catalyst **1-Cr** (50 mg, 0.0685 mmol Cr), NBu_4Br (73.2 mg, 0.2 mmol), propylene oxide (3.5 ml, 50 mmol) in a stainless steel autoclave. [d] Catalyst **1-Cr** (100 mg, 0.137 mmol Cr), NBu_4Br (146.5 mg, 0.4 mmol), propylene oxide (3.5 ml, 50 mmol). [e] Control experiments for the NBu_4Br co-catalyst carried out using propylene oxide (3.5 ml, 50 mmol) and NBu_4Br (549.6 mg, 1.5 mmol) for the experiment at 1 bar CO_2, 22 °C in 48 h, or using NBu_4Br (73.2 mg, 0.2 mmol) for the experiment at 100 °C, 20 bar CO_2 in 6 h (the values for this experiment are given in brackets). [f] Control experiments for the non-metalated species **1** using: propylene oxide (3.5 ml, 50 mmol) and: **1** (100 mg), NBu_4Br (146.5 mg, 0.4 mmol) for the experiment at 1 bar CO_2, 22 °C in 48 h, or **1** (50 mg), NBu_4Br (73.2 mg, 0.2 mmol) for the experiment at 20 bar CO_2, 100 °C in 16 h (the values for this experiment are given in brackets). [g] At 1 bar CO_2. [h] Reusing the catalyst recycled from the previous entry for three additional catalytic cycles. [i] Catalyst **1-Co** (50 mg, 0.0685 mmol Co), NBu_4Br (62.3 mg, 0.17 mmol), propylene oxide (3.5 ml, 50 mmol). [j] Catalyst **1-Co** (72 mg, 0.1 mmol Co), NBu_4Br (124.6 mg, 0.34 mmol), propylene oxide (3.5 ml, 50 mmol). [k] Catalyst **1-Co** (100 mg, 0.137 mmol Co), NBu_4Br (934.2 mg, 2.55 mmol), propylene oxide (3.5 ml, 50 mmol).

by Co(III),[25] Al,[26] Zn,[27] and Cu[26] salen complexes. The direction of this effect (*i.e.* towards higher or lower catalytic efficiency) depends on the metal center. In the case of homogeneous Co(III) salen catalysts, the presence of *t*-butyl substituents at the aromatic rings was found to have the effect of a strong increase in catalytic efficiency as compared to the analogous Co(III) complex with unsubstituted aromatic rings.[25] This is in a good agreement with what was observed for catalysts **1-Co** and **2-Co**. The presence of the AcO^- counter-ion in **2-Co** could also play a role in increasing its catalytic activity *versus* **1-Co** according to a comparative study for soluble Co(III) salen complexes.[25] However, on the basis of the results obtained for the homogeneous complexes, this effect is expected to be less pronounced than that of the substitution pattern at the phenyl rings of the scaffold. Assuming that the catalytic reaction takes place also within the pores of the POPs and not just on their exposed surface, the larger surface area of **2-Co** (965 $m^2\,g^{-1}$) compared to **1-Co** (370 $m^2\,g^{-1}$) might also play a significant role in ensuring higher accessibility of the active centers.

Remarkably, POPs **3-Cr** and **3-Co**,[12b] having respectively lower and larger surface area as compared to those of **1-Co** and **1-Cr** (and in the case of **3-Co** also a different counter-anion) displayed both higher TON values for the conversion of **4a** than **1-Co** and **1-Cr** (*cf.* in particular the performance of **1-Co**, **1-Cr** at 75 °C, Table 1, entries 4, 14 and the results reported by Chun *et al.* at 60 °C in ref. 12*b*). Taken together, these results indicate that the electronic effects generated by the substitution pattern of the salen scaffold may have a stronger influence on the catalytic activity than the surface area of the polymer.

We compared the catalytic performance of **1-Co** and **1-Cr** with that of other supported salen systems. Interestingly, the conversion of epoxide **4a** afforded by our catalysts in 16 h at 100 °C and 20 bar CO_2 (Table 1, entries 5, 15) is higher than that reported by Jiang *et al.* under comparable conditions (100 °C, 20 bar, 24 h) for a Ni(salphen) catalyst supported within a Cd-based MOF.[20k] The activity of the latter system is higher at slightly lower temperatures as it affords 80% **4a** conversion in 4 h at 80 °C and 20 bar CO_2 (see also Table 1, entries 4 and 14) but it is not reported under ambient conditions. Amongst the salen-based heterogeneous catalysts active under ambient conditions for the title reaction, it is worth mentioning a silica-supported single component Al–salen bimetallic catalyst by North *et al.*[18b] This system affords 86% **4a** conversion in 24 h (TOF = 0.7) at 26 °C and 1 bar CO_2 using a high catalyst loading (5 mol% Al *versus* 0.137 mol% Cr for **1-Cr**, Table 1, entry 3 and 0.2 mol% Co for **1-Co**, Table 1, entry 12). However, it does not require the addition of external nucleophiles. The preparation of such single component POPs for the cycloaddition of CO_2 to

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epoxides is highly desirable in order to fully exploit the potential of this novel catalyst design.

4. Conclusions

We report the application of novel POPs as heterogeneous catalysts for CO_2 conversion, and specifically, as porous solid matrices where catalytically active molecules are covalently integrated into the scaffold backbone. In the presented metal-osalen-based POPs, the coupled enhancement of catalyst lifetime and facile recyclability confirms the potential of POPs as novel matrices to immobilize small functional molecules into porous robust solids. The obtained catalytic results are compared with those reported for other salen-based POPs that have been employed as catalysts for the title reaction. It is worth highlighting that analogously as for the homogeneous catalysis, the electronic features of the salen backbone play a decisive role in catalysis, and can be amplified by the morphological properties of the synthesized POPs. In the light of the nearly infinite number of possibilities in terms of the choice of the salen scaffold, metal, counter-anion and polytopic linker, very active heterogeneous catalysts can be generated in the future for the fixation of CO_2, by its cycloaddition to epoxides to yield liquid organic carbonates.

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Notes and references

1 (*a*) Z.-Z. Yang, L.-N. He, J. Gao, A.-H. Liu and B. Yu, *Energy Environ. Sci.*, 2012, **5**, 6602; (*b*) S. H. Kim, K. H. Kim and S. H. Hong, *Angew. Chem., Int. Ed.*, 2014, **53**, 771.

2 (*a*) I. Omae, *Coord. Chem. Rev.*, 2012, **256**, 1384; (*b*) M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann and F. E. Kühn, *Angew. Chem., Int. Ed.*, 2011, **50**, 8510; (*c*) *Carbon Dioxide as Chemical Feedstock*, ed. M. Aresta, Wiley-VCH, Weinheim, 2010; (*d*) M. Mikkelsen, M. Jørgensen and F. C. Krebs, *Energy Environ. Sci.*, 2010, **3**, 43; (*e*) S. Y. T. Lee, A. A. Ghani, V. D'Elia, M. Cokoja, W. A. Herrmann, J.-M. Basset and F. E. Kühn, *New J. Chem.*, 2013, **37**, 3512.

3 (*a*) M. O. Sonnati, S. Amigoni, E. P. Taffin de Givenchy, T. Darmanin, O. Choulet and F. Guittard, *Green Chem.*, 2013, **15**, 283; (*b*) X.-B. Lu and D. J. Darensbourg, *Chem. Soc. Rev.*, 2012, **41**, 1462; (*c*) P. P. Pescarmona and M. Taherimehr, *Catal. Sci. Technol.*, 2012, **2**, 2169; (*d*) M. North, R. Pasquale and C. Young, *Green Chem.*, 2010, **12**, 1514; (*e*) B. Schäffner, F. Schäffner, S. P. Verevkin and A. Börner, *Chem. Rev.*, 2010, **110**, 4554; (*f*) T. Sakakura and K. Kohno, *Chem. Commun.*, 2009, 1312.

4 (*a*) A. Monassier, V. D'Elia, M. Cokoja, H. Dong, J. D. A. Pelletier, J.-M. Basset and F. E. Kühn, *ChemCatChem*, 2013, **5**, 1321; (*b*) M. E. Wilhelm, M. H. Anthofer, R. M. Reich, V. D'Elia, J.-M. Basset, W. A. Herrmann, M. Cokoja and F. E. Kühn, *Catal. Sci. Technol.*, 2014, **4**, 1638; (*c*) B. Dutta, J. Sofack-Kreutzer, A. A. Ghani, V. D'Elia, J. D. A. Pelletier, M. Cokoja, F. E. Kühn and J.-M. Basset, *Catal. Sci. Technol.*, 2014, **4**, 1534; (*d*) V. D'Elia, A. A. Ghani, A. Monassier, J. Sofack-Kreutzer, J. D. A. Pelletier, M. Drees, S. V. C. Vummaleti, A. Poater, L. Cavallo, M. Cokoja, J.-M. Basset and F. E. Kühn, *Chem.–Eur. J.*, 2014, **20**, 11870; (*e*) V. D'Elia, J. D. A. Pelletier and J.-M. Basset, *ChemCatChem*, 2015, **7**, 1906; (*f*) A. Barthel, Y. Saih, M. Gimenez, J. D. A. Pelletier, F. E. Kühn, V. D'Elia and J. M. Basset, *Green Chem.*, 2016, DOI: 10.1039/C5GC03007B.

5 (*a*) W.-Y. Gao, Y. Chen, Y. Niu, K. Williams, L. Cash, P. J. Perez, L. Wojtas, J. Cai, Y.-S. Chen and S. Ma, *Angew. Chem., Int. Ed.*, 2014, **53**, 2615; (*b*) H. V. Babu and K. Muralidharan, *Dalton Trans.*, 2013, **42**, 1238; (*c*) C. J. Whiteoak, E. Martin, M. M. Belmonte, J. Benet-Buchholz and A. W. Kleij, *Adv. Synth. Catal.*, 2012, **354**, 469; (*d*) J. A. Castro-Osma, A. L. Sanchez, M. North, A. Otero and P. Villuendas, *Catal. Sci. Technol.*, 2012, **2**, 1021; (*e*) Y. Yang, Y. Hayashi, Y. Fujii, T. Nagano, Y. Kita, T. Ohshima, J. Okuda and K. Mashima, *Catal. Sci. Technol.*, 2012, **2**, 509; (*f*) A. Buchard, M. R. Kember, K. G. Sandeman and C. K. Williams, *Chem. Commun.*, 2011, **47**, 212; (*g*) W. Clegg, R. W. Harrington, M. North and R. Pasquale, *Chem.–Eur. J.*, 2010, **16**, 6828; (*h*) S. F. Yin and S. Shimada, *Chem. Commun.*, 2009, 1136; (*i*) J. Meléndez, M. North and R. Pasquale, *Eur. J. Inorg. Chem.*, 2007, 3323.

6 For recent reviews, see: (*a*) U. H. F. Bunz, K. Seehafer, F. L. Geyer, M. Bender, I. Braun, E. Smarsly and J. Freudenberg, *Macromol. Rapid Commun.*, 2014, **35**, 1466; (*b*) M. L. Foo, R. Matsuda and S. Kitagawa, *Chem. Mater.*, 2014, **26**, 310; (*c*) Q. Liu, Z. Tang, M. Wu and Z. Zhou, *Polym. Int.*, 2014, **63**, 381; (*d*) X. Zou, H. Rena and G. Zhu, *Chem. Commun.*, 2013, **49**, 3925; (*e*) Y. Xu, S. Jin, H. Xu, A. Nagai and D. Jiang, *Chem. Soc. Rev.*, 2013, **42**, 8012; (*f*) S. Xu, Y. Luo and B. Tan, *Macromol. Rapid Commun.*, 2013, **34**, 471; (*g*) R. Dawson, A. I. Cooper and D. J. Adams, *Prog. Polym. Sci.*, 2012, **37**, 530.

7 (*a*) Z. Chang, D.-S. Zhang, Q. Chen and X.-H. Bu, *Phys. Chem. Chem. Phys.*, 2013, **15**, 5430; (*b*) F. Vilela, K. Zhang and M. Antonietti, *Energy Environ. Sci.*, 2012, **5**, 7819for selected recent examples, see: (*c*) H. Li, Z. Li, Y. Zhang, X. Luo, H. Xia, X. Liu and Y. Mua, *RSC Adv.*, 2014, **4**, 37767; (*d*) S. J. Ren, R. Dawson, A. Laybourn, J. X. Jiang, Y. Khimyak, D. J. Adams and A. I. Cooper, *Polym. Chem.*, 2012, **3**, 928; (*e*) R. Dawson, D. J. Adams and A. I. Cooper, *Chem. Sci.*, 2011, **2**, 1173; (*f*) W. Lu, D. Y. D. Zhao, C. I. Schilling, O. Plietzsch, T. Muller, S. Bräse, J. Guenther, J. Blümel, R. Krishna, Z. Li and H.-C. Zhou, *Chem. Mater.*, 2010, **22**, 5964; (*g*) S. W. Yuan, B. Dorney, D. White, S. Kirklin, P. Zapol, L. P. Yu and D. J. Liu, *Chem. Commun.*, 2010, **46**, 4547; (*h*) J. Chun, S. Kang, N. Park, E. J. Park, X. Jin, K.-D. Kim, H. O. Seo, S. M. Lee, H. J. Kim, W. H. Kwon, Y.-K. Park, J. M. Kim, Y. D. Kim and S. U. Son, *J. Am. Chem. Soc.*, 2014, **136**, 6786.

8 For selected recent examples, see: (*a*) C. Gu, Y. C. Chen, Z. B. Zhang, S. F. Xue, S. H. Sun, K. Zhang, C. M. Zhong,

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H. H. Zhang, Y. Y. Pan, Y. Lv, Y. Q. Yang, F. H. Li, S. B. Zhang, F. Huang and Y. G. Ma, *Adv. Mater.*, 2013, **25**, 3443; (*b*) Y. Xu, A. Nagai and D. Jiang, *Chem. Commun.*, 2013, **49**, 1591; (*c*) Y. H. Xu, L. Chen, Z. Q. Guo, A. Nagai and D. Jiang, *J. Am. Chem. Soc.*, 2011, **133**, 17622; (*d*) J.-X. Jiang, A. Trewin, D. J. Adams and A. I. Cooper, *Chem. Sci.*, 2011, **2**, 1777; (*e*) L. Chen, Y. Honsho, S. Seki and D. Jiang, *J. Am. Chem. Soc.*, 2010, **132**, 6742.

9 (*a*) X. Liu, S. A. Y. Zhang, X. Luo, H. Xia, H. Lia and Y. Mu, *RSC Adv.*, 2014, **4**, 6447; (*b*) N. Kang, J. H. Park, M. Jin, N. Park, S. M. Lee, H. J. Kim, J. M. Kim and S. U. Son, *J. Am. Chem. Soc.*, 2013, **135**, 19115; (*c*) A. Modak, M. Pramanik, S. Inagaki and A. Bhaumik, *J. Mater. Chem. A*, 2014, **2**, 11642; (*d*) W.-K. An, M.-Y. Han, C.-A. Wang, S.-M. Yu, Y. Zhang, S. Bai and W. Wang, *Chem.–Eur. J.*, 2014, **20**, 11019; (*e*) J. Schmidt, D. S. Kundu, S. Blechert and A. Thomas, *Chem. Commun.*, 2014, **50**, 3347; (*f*) L. Li, H. Zhao, J. Wang and R. Wang, *ACS Nano*, 2014, **8**, 5352; (*g*) H. Li, B. Xu, X. Liu, S. A. C. He, H. Xia and Y. Mu, *J. Mater. Chem. A*, 2013, **1**, 14108.

10 (*a*) C. Baleizao and H. Garcia, *Chem. Soc. Rev.*, 2006, **106**, 3987; (*b*) P. G. Cozzi, *Chem. Rev.*, 2004, **33**, 410.

11 A. Decortes, A. M. Castilla and A. W. Kleij, *Angew. Chem., Int. Ed.*, 2010, **49**, 9822.

12 (*a*) Y. Xie, T.-T. Wang, X.-H. Liu, K. Zou and W.-Q. Deng, *Nat. Commun.*, 2013, **4**, 1960; (*b*) J. Chun, S. Kang, N. Kang, S. M. Lee, H. J. Kim and S. U. Son, *J. Mater. Chem. A*, 2013, **1**, 5517.

13 A. R. Silva, T. Mourão and J. Rocha, *Catal. Today*, 2013, 81.

14 V. Guillerm, Ł. J. Weseliński, M. H. Alkordi, M. I. H. Mohideen, Y. Belmabkhout, A. J. Cairns and M. Eddaoudi, *Chem. Commun.*, 2014, **50**, 1937.

15 K. P. Bryliakov and E. P. Talsi, *Inorg.Chem.*, 2003, **42**, 7258.

16 (*a*) I. Grohmann, E. Kemnitz, A. Lippitz and W. E. S. Unger, *Surf. Interface Anal.*, 1995, **23**, 887; (*b*) T. Gross, D. Treu, E. Ünveren, E. Kemnitz and W. E. S. Unger, *Surf. Sci. Spectra*, 2008, **15**, 77; (*c*) M. Aronniemi, J. Sainio and J. Lahtinen, *Surf. Sci.*, 2005, **578**, 108.

17 (*a*) T. J. Chuang, C. R. Bridle and D. W. Rice, *Surf. Sci.*, 1976, **59**, 413; (*b*) C. A. F. Vaz, D. Prabhakaran, E. I. Altman and V. E. Henrich, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2009, **80**, 155457.

18 (*a*) W. L. Dai, S. L. Luo, S. F. Yin and C. T. Au, *Appl. Catal., A*, 2009, **366**, 2; (*b*) J. Melendez, M. North, P. Villuendas and C. Young, *Dalton Trans.*, 2011, **40**, 3885; (*c*) M. North, P. Villuendas and C. Young, *Chem.–Eur. J.*, 2009, **15**, 11454; (*d*) F. Jutz, J. D. Grunwaldt and A. Baiker, *J. Mol. Catal. A: Chem.*, 2008, **279**, 94; (*e*) M. Ramin, F. Jutz, J. D. Grunwaldt and A. Baiker, *J. Mol. Catal. A: Chem.*, 2005, **242**, 32; (*f*) M. Alvaro, C. Baleizao, E. Carbonell, M. El Ghoul, H. Garcia and B. Gigante, *Tetrahedron*, 2005, **61**, 12131; (*g*) M. Alvaro, C. Baleizao, D. Das, E. Carbonell and H. Garcia, *J. Catal.*, 2004, **228**, 254; (*h*) X. B. Lu, J. H. Xiu, R. He, K. Jin, L. M. Luo and X. J. Feng, *Appl. Catal., A*, 2004, **275**, 73.

19 (*a*) J. Meléndez, M. North and P. Villuendas, *Chem. Commun.*, 2009, 2577; (*b*) V. D'Elia, H. Dong, A. J. Rossini, C. M. Widdifield, S. V. C. Vummaleti, Y. Minenkov, A. Poater, E. Abou-Hamad, J. D. A. Pelletier, L. Cavallo, L. Emsley and J.-M. Basset, *J. Am. Chem. Soc.*, 2015, **137**, 7728.

20 (*a*) V. Guillerm, Ł. J. Weseliński, Y. Belmabkhout, A. J. Cairns, V. D'Elia, L. Wojtas, K. Adil and M. Eddaoudi, *Nat. Chem.*, 2014, **6**, 673; (*b*) A. C. Kathalikkattil, D.-W. Kim, J. Tharun, H.-G. Soek, R. Roshan and D.-W. Park, *Green Chem.*, 2014, **16**, 1607; (*c*) A. C. Kathalikkattil, R. Roshan, J. Tharun, H. G. Soek, H.-S. Ryu and D.-W. Park, *ChemCatChem*, 2014, **6**, 284; (*d*) X. Huang, Y. Chen, Z. Lin, X. Ren, Y. Song, Z. Xu, X. Dong, X. Li, C. Hu and B. Wang, *Chem. Commun.*, 2014, **50**, 2624; (*e*) D. Feng, W.-C. Chung, Z. Wei, Z.-Y. Gu, H.-L. Jiang, Y.-P. Chen, D. J. Darensbourg and H.-C. Zhou, *J. Am. Chem. Soc.*, 2013, **135**, 17105; (*f*) O. V. Zalomaeva, A. M. Chibiryaev, K. A. Kovalenko, O. A. Kholdeeva, B. S. Balzhinimaev and V. P. Fedin, *J. Catal.*, 2013, **298**, 179; (*g*) Y. Ren, X. Cheng, S. Yang, C. Qi, H. Jiang and Q. Mao, *Dalton Trans.*, 2013, **42**, 9930; (*h*) X. Zhou, Y. Zhang, X. Yang, L. Zhao and G. Wang, *J. Mol. Catal. A: Chem.*, 2012, **361–362**, 12; (*i*) T. Lescouet, C. Chizallet and D. Farrusseng, *ChemCatChem*, 2012, **4**, 1725; (*j*) J. Song, Z. Zhang, S. Hu, T. Wu, T. Jiang and B. Han, *Green Chem.*, 2009, **11**, 1031; (*k*) Y. Ren, Y. Shi, J. Chen, S. Yang, C. Qi and H. Jiang, *RSC Adv.*, 2013, **3**, 2167.

21 J. Roeser, K. Kailasam and A. Thomas, *ChemSusChem*, 2012, **5**, 1793.

22 (*a*) C. J. Whiteoak, A. Nova, F. Maseras and A. W. Kleij, *ChemSusChem*, 2012, **5**, 2032; (*b*) Y.-M. Shen, W.-L. Duan and M. Shi, *Eur. J. Org. Chem.*, 2004, 3080.

23 (*a*) L. Chiang, L. E. N. Allan, J. Alcantara, M. C. P. Wang, T. Storr and M. P. Shaver, *Dalton Trans.*, 2014, **43**, 4295; (*b*) L. Cavallo and H. Jacobsen, *J. Org. Chem.*, 2003, **68**, 6202.

24 F. Castro-Gomez, G. Salassa, A. W. Kleij and C. Bo, *Chem.–Eur. J.*, 2013, **19**, 6289.

25 T. Chang, H. Jing, L. Jin and W. Qiu, *J. Mol. Catal. A: Chem.*, 2007, **264**, 241.

26 X.-B. Lu, Y.-J. Zhang, K. Jin, L.-M. Luo and H. Wang, *J. Catal.*, 2004, **227**, 537.

27 Y.-M. Shen, W.-L. Duan and M. Shi, *J. Org. Chem.*, 2003, **68**, 1559.

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