Tethering of bi-nuclear complexes to SBA-15 and their application in CO2 hydrogenation

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Abstract

Two bimetallic cryptates (containing Cu and Co), which have previously been shown to react with and activate atmospheric CO2, have been tethered to modified mesoporous SiO2 and their activities in promoting the CO2 + H2 reaction has been analysed. The cryptates have been tethered to –C3H6Cl modified SBA-15 through a condensation reaction between surface alkyl chlorides and 2° amines of the ligands releasing HCl and forming a 3° amine. The materials have been characterised using BET, TGA, FTIR and elemental analysis and their activity in promoting the CO2 + H2 reaction has been tested under batch reactor conditions. Co ions appear to selectively populate the medal sites of the tethered ligands while Cu ions appear to deposit on the surface as Cu(BF4)2 salts. The composite materials generate CO and CH4 from the CO2 + H2 mixtures. Co-containing catalysts are more effective than the Cu analogues in promoting the reaction.

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Introduction
The conversion of CO₂ into useful fuels and chemicals would immediately ameliorate two of the most pressing issues associated with the combustion of fossil fuels, i.e. it would decrease emissions of CO₂ (a greenhouse gas) and also form replacement fuels and chemical feedstocks which are currently produced from depleting reservoirs of fossil fuels.

Several researchers have studied homogeneous,¹ heterogeneous,² and enzymatic,³ catalysts that use H₂ to reduce CO₂ to carbon monoxide, methanol, formate and oxalate ions, organic acids and methane. The catalysts range from variations of the traditional methanol synthesis catalyst Cu/ZnO,⁴ to homogeneous organometallic complexes,⁵ and vanadium containing Cu materials.⁶ Synthesis of hydrocarbons rather than CH₃OH from CO₂ hydrogenation has also been investigated over hybrid catalysts consisting of Cu/ZnO/ZrO₂ and zeolites (MFI and SAPO).⁷

Furthermore there has been significant research effort put into catalysts to promote to both photo-chemical⁸⁻¹¹ and electro-chemical reduction of CO₂.¹²⁻¹⁴

Metal complexes that activate CO₂ towards hydrogenation are also known in both homogenous and heterogeneous systems and these have been studied and reviewed.⁵ Specifically in relation to the current work, Rh complexes with bidentate chelating phosphane ligands,¹⁵ Ir(III)-Pincer complexes¹⁶ and immobilized Ru complexes¹⁷ have all been examined for activity in the H₂ + CO₂ reaction under different conditions of temperature and pressure. Formic acid is the main product of interest observed during these studies.
Although the reaction of CO₂ with hydroxide to generate hydrogen carbonate ions or carbonate ions is extremely slow in the absence of catalysis, there have been many examples of CO₂ uptake followed by this reaction in dinuclear transition metal systems.[18, 19]

Azacryptate complexes containing pairs of metal ions from the first transition metal series have been shown to take up CO₂ spontaneously from the atmosphere.[20, 21] This process occurs in a wet solvent system and the CO₂ is fixed as a carbonate bridge between the metal centres.

Spontaneous fixation of CO₂ in this way has also been observed in a limited number of other dinuclear macrocyclic systems,[22, 23] but such behaviour is very rare. Although a number of acyclic transition metal complexes will fix CO₂ as carbonate, this is typically not in such a strained environment as when it is tethered between two bound metal ions in a cage structure. This confers two important properties on the bound carbonate. Firstly the C-O bonds will be stretched between the coordinated metals and the extent of this strain can be modulated by changing the ligand size. In addition the C-O bonds will be no longer equivalent, as there is additional double bond character between the central carbon and the uncoordinated oxygen presumably enhancing the reactivity of this bond. Early indications of such enhanced reactivity have been manifest by insertion of methanol into the carbonato-bound azacrytates, forming a methyl carbonato bridged complex.[20] This demonstrates activation of the bound carbonate towards nucleophilic attack which we have attempted to exploit in this work by using these complexes as CO₂ reduction catalysts. When these complexes have been used as homogeneous catalysts in the
CO$_2$ + H$_2$ reaction minor mounts of formic acid and methanol have been noted as products.

Obviously, notwithstanding this unique reactivity, one of the general problems associated with the use of organometallic complexes as catalysts is that the catalysts are isophasic with the reactants and products and therefore removal of the catalyst from the reaction mixture and recycling of the catalyst becomes difficult.

There has been a significant body of work in the immobilization of molecular homogeneous catalysts onto solid supports. In general, this “heterogenisation” has taken place using differential catalyst solubility approaches,$^{[24-25]}$ as well as through the use of non-covalent,$^{[26-27]}$ or covalent,$^{[27-33]}$ interactions between the molecular catalyst and the surface of the solid material either following modification of the surface of the solid or the catalytic material or both.

Regarding tethering, there are several examples of the tethering of molecular complexes through modification of the complex ligands, and the complementary modification of the surface.$^{[26]}$

In the current work we take a different approach to the hetrogenization of the bimetallic cryptand materials onto mesoporous SiO$_2$, i.e. instead of preparing and tethering the bimetallic cryptate material we tether the cryptand to the surface using a condensation reaction and subsequently attempt to populate this tethered cryptand with the metal ions of interest through treatment with solutions of CuBF$_4$ and CoBF$_4$.

In the present work, we have prepared mesoporous silica (SBA-15) supported binuclear cryptates by covalently tethering these complexes onto modified mesoporous SiO$_2$ materials.
Herein we report the preparation and characterisation of the modified mesoporous materials, the tethering of the complexes to the modified silica, characterisations of the modified materials and the application of the tethered cryptates in the CO$_2$ hydrogenation reaction.

Results and Discussion

Materials Characterisation

Characterisation of synthesised ligands: The cryptands formed were characterised using microanalysis, FTIR and $^1$H and $^{13}$C NMR. These characterisations confirm the structure reported previously.\[^{21}\]

Textural characteristics and [Cl]: The parent SBA-15 material and SBA-15-Cl were white powders, while the SBA-15-Cl-crypt material was yellow. Addition of the metal ions to the nanocomposite resulted in some colour changes, i.e. Co-SBA–15–Cl was a very pale brown and Cu-SBA–15–Cl was light green. Small angle XRD (see Figure S1 for representative examples) and TEM measurements (see Figure S2 for representative examples) have confirmed the mesoporous structure of the SBA-15 and the Cl-modified SBA-15. The small angle XRD profiles for the cryptand-containing materials show that this structure is significantly compromised following incorporation of the crypt (and subsequent incorporation of the metal ions). This is confirmed by TEM analysis,\[^{34}\] which shows the hexagonal structure – while still being intact in the presence of the metal-loaded crypt – is considerably more disordered than was the case of the parent SBA-15 and the R-Cl modified material (Figure S2).
These characterisations are confirmed by BET measurements (see Table 1) which show that both the surface area and the pore size are affected by the presence of the tethers and the tethered crypt materials. The surface area decreased from ~620 m² g⁻¹ in the case of SBA-15 to ~205 m² g⁻¹ following modification with the R-Cl groups. Tethering the crypt to the latter decreased the surface area further to ~80 m² g⁻¹. Similar effects are noted for the pore sizes, i.e. they decrease once the tethers and the crypts are incorporated into the material (from ~34 nm to ~18 nm). Addition of the metal salts to these materials in attempts to populate the metallic sites in the tethered ligands further decreased the surface areas and the pore sizes (see Table 1). This results in the pore sizes being significantly smaller than in the unmodified SiO₂ but still wide enough to comfortably allow the ingress and egress of relatively large molecules to the internal catalyst surface.

Analysis of the Cl content of the synthesised materials confirms the successful modification of the SiO₂ with the alkyl chloride tether (the SBA-15-Cl material contains 4.46% Cl). This suggests the SiO₂ was modified with ~1300 μmol g⁻¹ of alkyl chloride. CHN analysis confirmed the expected C:H:Cl ratio of the tethered material.

The level of Cl in the material containing the crypt is much decreased on this value, ([Cl] in the composite material was measured as 0.36% following condensation of HCl during the tethering reaction) confirming covalent tethering of the cryptand. This suggests that of the ~1300 μmol of tether g⁻¹ of catalyst that a relatively small fraction did not condense with the polyamino cryptand and remained
un-reacted while the majority was involved in the condensation and tethering reaction. Again CHN analysis confirmed the approximate loadings of crypt noted in TGA (see later) and the C:H:N ratio was close to the expected values (C:H:N expected was 4.5 : 6 : 1 and observed was 4.52 : 6.65 : 1) variations are accounted for by the presence of the linker portion of the tether and the fact that we are not able to estimate the number of tethers per crypt molecule.

<table>
<thead>
<tr>
<th></th>
<th>Surface area / m² g⁻¹</th>
<th>Pore size / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>621</td>
<td>34</td>
</tr>
<tr>
<td>SBA-15-Cl</td>
<td>206</td>
<td>19</td>
</tr>
<tr>
<td>SBA-15-Cl-Crypt</td>
<td>82</td>
<td>18</td>
</tr>
<tr>
<td>Co SBA-15-Crypt</td>
<td>75</td>
<td>15</td>
</tr>
<tr>
<td>Cu SBA-15-Crypt</td>
<td>72</td>
<td>15</td>
</tr>
</tbody>
</table>
Elemental analysis confirms a loading of 0.08% Co and a significantly higher loading of 2.2% Cu. The latter figure, and the light green colour of the formed material, suggest deposition of Cu(BF₄)₂ onto the support.

**FTIR Analysis**

Figure 1 shows the DRIFTS spectra of unmodified SBA-15 and SBA-15-Cl. The modification of the parent SBA-15 with the propyl-chloride tether is clearly shown by the disappearance of the sharp OH peak at 3750 cm⁻¹ (following condensation of the 3-Chloro propyltriethoxysilane with the surface OH groups) and the appearance of CH stretching peaks between 3000 cm⁻¹ and 2800 cm⁻¹.

Tethering the ligand onto the surface (Figure S3) decreases the intensity of the IR spectra obtained from the materials. Aliphatic C-H stretches are still visible (2800-3000 cm⁻¹) but the presence of aromatic CH and C-C vibrations are not clear. No specific peaks due to the presence of 2° amines of the cryptand can be determined (recall significant numbers of these would be removed through the condensation reaction). Adding Co²⁺ or Cu²⁺ to the nanocomposite material (Figure S3) further decreases the %T in the FTIR spectra and again no distinguishing characteristic bands of the aromatic or amine (or BF₄⁻) species can be discerned.
Figure 1. FTIR profiles of SBA-15 (▲) and SBA-15-Cl (■).

Thermogravimetric analysis

Figure 2 shows DTGA plots recorded from Cl-modified SBA-15 and the cryptand tethered onto SBA-15 in the absence and presence of metal ions.

During TGA of the Cl-containing materials HCl was recorded in the exit gas suggesting that it does not remain on the catalyst following the combustion reaction. A total mass loss of 14% was recorded following treatment of the Cl-modified SBA-15. The tether begins to combust at approximately 120 °C and its maximum rate of combustion is seen at ~ 170 °C. CHN analysis (3.50 5 C, 0.86% H), Cl analysis (4.46 % Cl) confirm a loading of tether in the range 1150 – 1300 μmol g⁻¹; the mass loss seen in TGA is higher (~13%) than these figures would suggest but it must be remembered that this also accounts for the desorption of physisorbed H₂O at lower temperatures and dehydration via surface de-hydroxylation at higher temperatures.
The TGA profile of the tethered ligand is dramatically different to both that of the tether alone and that of the ligand alone (see below), indicating that the interaction between the ligand and the tether has modified the combustion properties of both the ligand and the tether. In the case of the latter this would be related to the removal of the Cl atom and in the former case it might be related to localized exotherms during the TGA experiment. In this case, i.e. TGA of the tethered ligand, approximately 50% of the mass of the composite is lost through combustion (recall this also represents dehydration of the material). Removal of the organic material begins at ~ 200 °C and two regions of reactivity are noted, one between 300 °C and 400 °C and a second between 500 °C and 600 °C. The mass loss and associated differential TG profile confirm that significant amounts of the ligand had been tethered to the functionalised SiO₂ material and that the nanocomposite material is stable at temperatures up to 200 °C. CHN analysis suggests that ~44% of the mass of the composite material is organic (32.86% C, 4.03 % H and 8.48% N).

Given the measured concentrations of R-Cl linker on the surface and the overall concentrations of organic material, the concentration of tethered material can be estimated. With the molecular mass of the ligand being 598 g mol⁻¹ we can say that the loading of the ligand on the modified SiO₂ is of the order of 720 μmol g⁻¹.
Assuming that each tethered ligand molecule can accommodate two metal ions,[20, 21] this gives a metal ion capacity of the material of \(~1440\ \mu\text{mol g}^{-1}\). This translates to a theoretical loading of \(~0.09\ %\ \text{Cu}\) and \(~0.08\ %\ \text{Co}\). Elemental analysis shows this for Co content (0.08 %) following treatment of the nanocomposite with cobalt tetrafluoroborate. The Cu loading was found to be significantly higher (2.2 %). This suggests that when the composite was treated with Co$^{2+}$ cations these selectively populated the metal ion sites within the tethered ligand (forming a relatively active catalyst) while the treatment with solutions of copper tetrafluoroborate did not simply populate Cu ions into the metal sites of the material but also precipitated the Cu salt onto the surface. The formed material is significantly less active than the cobalt analogue (see later).

TGA of the non-tethered ligand (not shown) shows two combustion events, one centred at 350 °C and a second centred at 550 °C. The ligand is completely
combusted by 640 °C. These results show that tethering onto the SiO₂ material has destabilized the cryptand somewhat (the tethered ligand begins to combust at 200 °C and is fully combusted by 600 °C).

When the modified SiO₂ materials which had been condensed with the ligand and treated with solutions of either Co or Cu salts are analysed using TGA the resultant profiles are significantly different to those derived from the combustion of the cryptand or the tethered cryptand (see figure 2). The approximate weight losses are comparable to each other (with ~ 50% being lost in both cases).

When Cu is the added metal, combustion begins at ~ 215 °C. There are two very distinct peaks in the DTGA profiles at 370 °C and 405 °C. The presence of Cu ions has further catalysed the combustion of the tethered crypt with combustion being complete by 500°C (recall in the absence of metal the combustion was not complete until ~ 600 °C). Recall there are significant amounts of Cu(BF₄)₂ on this catalyst but while this salt decomposes during TGA its principal decomposition is at a temperature of 230 °C (see figure S4).

When the added metal ions were Co²⁺, combustion begins at 270 °C and is complete at ~ 480 °C. Again approximately 50% of the composite material is removed through combustion and again combustion is catalysed in the presence of the metal ions. One difference between this profile and those of the unmodified tethered ligand and the Cu containing tethered ligand is that the distinct peaks evident in the latter two cases are not as evident here. This suggests that the nanocomposite material is more heterogeneous in nature, i.e. has a range of
stabilities, following the addition of Co than it has following the addition of Cu. It should be recalled that there are significant amounts of Cu(BF$_4$)$_2$ on the former material.

**Catalytic Activity**

Catalytic activity was measured in a 300 mL Parr reactor containing 150 mL cyclohexane solvent and 250 mg of tethered catalyst material. The reactor was charged at room temperature with CO$_2$, H$_2$ (7.31 mmol H$_2$ and 3.05 mmol CO$_2$) and Ar to a pressure of 45 bar. The temperature was subsequently raised to either 150 °C or 200 °C and held here for 4 h. From the TGA data presented above the tethered catalysts are known to be stable at these temperatures.

No products were noted from the CO$_2$ + H$_2$ reaction mixture when the reactor had no catalyst present, or when the SBA-15, the SBA-15-Cl or the Ligand-SBA-15-Cl materials were used as catalysts.
No CH$_3$OH, CH$_2$O or HCO$_2$H (or any C$_2$ or higher species) were found in the liquid phase. Small but measurable amounts of formate (0.02 mmol), acetate (0.02 mmol) and oxalate (0.08 mmol) anions were measured (using ion chromatography) in the reaction solvent when the Cu catalyst was used while trace amounts of formate and oxalate anions were seen when the Co catalyst was used.

Analysis of the gas phase shows the production of CH$_4$ and CO during the reaction (see Figure 3(a)). In the case of the Cu-containing catalysts CH$_4$ was the
major product with [CO] being below the levels of detection of the GC. Between 0.2 and 0.4 mmol of CH$_4$ was produced during the reaction. When the Co-containing tethered cryptate was used, the production of both CO and CH$_4$ was noted with slightly more CO than CH$_4$ formed.

When the Co or Cu–SBA-15-Cl nanocomposite materials were used, removal of CO$_2$ and H$_2$ from the gas phase was noted. Figure 3(b) shows the extent of removal of CO$_2$ and H$_2$ following the 4 h reaction at 150 °C and 200 °C. These figures are based on the levels of CO$_2$ and H$_2$ detected in the gas phase following their charge into the reactor and after 4 h. This change in [CO$_2$] is influenced by factors such as solubility and surface adsorption as well as reactivity. This explains why in certain cases lower “conversions” are seen at higher temperatures.

In any case, it is clear that of the CO$_2$ and the H$_2$ dosed to the reactor at the beginning of the experiment significant fractions are removed during the reactions. Regarding H$_2$ reaction, approximately 14% of the H$_2$ is removed from the gas phase following reaction at 150 °C while ~ 4% is removed at 200 °C. This behaviour was similar for both catalysts.

When the removal of CO$_2$ is compared to this, it is clear that the amounts removed were higher in the case of the Co-containing catalyst (75% – 45%) than over the Cu-containing catalyst (20% – 30%). This correlates with the increased formation of products over this material. However, it is clear (notwithstanding any effects of solubility of CO$_2$ in cyclohexane), that a carbon balance has not been achieved, i.e. there is an order of magnitude fewer products observed (0.3 – 0.4
mmol) than there is CO\textsubscript{2} removed from the system (1.5 mmol). The numbers in parentheses represent the extent of reaction over the Co catalyst following the 200 °C reaction. Since we are unable to detect the formation of any dissolved product this suggests that there may be material adsorbed on the catalyst.

We can assume that a portion of this “missing” CO\textsubscript{2} is due to solubility within the reaction mixture but the difference between the amount removed when the Co catalyst is used (2.25 – 1.5 mmol at 150 and 200 °C respectively) relative to when the Cu material is used (0.6 – 0.9 mmol 150 and 200 °C respectively) cannot be related solely to solubility and must in some way relate to reactivity.

Given the mass of catalyst charged to the reactor and the loading of tether g\textsuperscript{-1} of catalyst we can say there are ~ 0.18 mmol of tether in the reactor at the commencement of the catalytic reaction. For the reaction over the Co catalyst at 200 °C, 1.5 mmol of CO\textsubscript{2} are removed from the gas phase. A portion of this (0.4 mmol) was converted to CO and CH\textsubscript{4}, and the remainder (1.1 mmol) was either solubilised or adsorbed onto the catalyst.

In the reaction over the Cu-based catalyst 0.9 mmol CO\textsubscript{2} were removed and ~ 0.4 mmol CH\textsubscript{4} formed. If we approximate the solubilised fraction to be the 0.5 mmol in the difference (from characterisation of post reaction catalysts there is very little adsorbed on the Cu catalyst - see later) and assume solubility of CO\textsubscript{2} in both reactions is the same then there are approximately 0.6 mmol of “missing” CO\textsubscript{2} in the Co-catalyed reaction This can be accounted for through the formation of stoichiometric adduct between the ligand and the CO\textsubscript{2} (recall there are 8 N atoms
per ligand and that several of these may be available for the formation of carbamate species.\textsuperscript{[35]}

**Characterisations of post-reaction catalysts**

In an attempt to determine whether any identifiable organic material had been left on the solid catalysts post reaction (and to characterise any such deposit) TGA and FTIR characterisations were carried out (see figures 4 and S5).

The DTGA profile (figure S5) of the Co-containing catalyst (post-reaction) has a similar shape to the analogous material tested prior to reaction, i.e. the combustible material is relatively heterogeneous in nature. The combustion is slightly delayed to a higher temperature and there is an increase in the amount of combustible material on the catalyst, i.e. 52.3% mass decrease post reaction compared to a 50.5% mass decrease prior to reaction. This result suggests that there is some oxidisable / decomposable material deposited on the catalyst during reaction. In the case of the Cu-containing material the amount of removable material has increased from 50.0% to 50.3%. This is a far lower increase and suggests, assuming all other factors are equal, that there is a negligible amount of material adsorbed on this catalyst. This correlates with the increased amount of CO\textsubscript{2} removed from the gas phase over the Co catalysts when compared to the Cu catalyst.
The FTIR (Figure 4) of the post reaction material (upper plots) shows some discernable differences in the spectra of the catalyst before and after reaction. Extra peaks are visible at energies of 1687 cm\(^{-1}\) and 2856 cm\(^{-1}\) which are suggestive of the formation of a carbamate on the catalyst surface. This may have formed following the reaction between CO\(_2\) and the amines in the tethered cryptate. Such reactivity has been previously reported in similar systems.\(^{[35]}\)

**Conclusion**

In this work we have prepared a nano-composite material consisting of a bimetallic (Co or Cu) cryptate tethered to a functionalised mesoporous SiO\(_2\) solid support. These cryptates have previously been shown to both fix and activate atmospheric CO\(_2\) towards reaction. We have characterised the composites and applied them as catalysts in the CO\(_2\) + H\(_2\) reaction.
The cryptate was tethered to modified SiO₂ through a condensation reaction between a surface alkyl halide and a 2° amine. The tethering was confirmed by both FTIR and TGA and we have demonstrated that approximately 50% of the composite material was composed of tethered ligand.

Both materials showed a certain activity in promoting the reduction of CO₂. The Cu-containing catalysts produced CH₄ as a primary product while the Co-containing catalysts produced both CO and CH₄ as products (with a slightly higher selectivity to CO). These activities are different to what would have been expected based on the previously observed chemistries of the cryptate materials in solution (where amounts of formic acid and methanol have been observed) and the activity of the individual crystalline complexes (where nucleophilic activation of CO₂ was observed).

Following the reaction a carbon balance was not achieved and this may be due to the formation of a CO₂-containing deposit on the catalyst. The extent of this deposit (as analysed by TGA) was relatively significant on the Co material and negligible on the Cu-containing catalysts. The deposited material showed FTIR bands at 1687 cm⁻¹ and 2856 cm⁻¹ suggesting it may be a carbamate species.

Experimental Section

**Preparation of cryptand ligands:** The synthesis and characterisation of the cryptate materials (see Figure 5) has been previously published.[21] In the preparation of the composite materials used in this work the ligands are synthesised
and tethered to modified mesoporous SiO$_2$ and subsequently the metal ions are added to form the final tethered binuclear cryptate material.

The ligands are synthesised as follows. Isophthalaldehyde (1.682 g, 12.5 mmol) was dissolved in methanol (300 mL). This was set to reflux under an atmosphere of nitrogen. When reflux was reached tris(2-aminoethyl) amine (1.222 g, 8.4 mmol) was added via syringe over a period of one minute. The solution was then left to reflux overnight. Sodium borohydride (2.4 g, 63 mmol) was added in small amounts over a period of approximately one hour. The solution was then left to reflux for a further three hours. After this time had elapsed the solution was cooled to room temperature and stirred for a further two days. The solution was then filtered and the solvent removed leaving a cream/yellow residue. This was taken up in a 2.5 M solution of sodium hydroxide. The organic product was then extracted using chloroform (3 x 50 mL). This was then dried over magnesium sulphate and the solvent was removed. This yielded yellow oil. This oil was left to dry under high vacuum for three days and a yellow waxy solid was obtained in 90 % yield.

These ligands, following characterisation using FTIR, microanalysis and NMR, were subsequently tethered to modified SBA-15 materials. The preparation and modification of the SBA-15 and the tethering of the cryptands thereon is discussed below.
Figure 5. (a) Synthesis of Polyamino Cryptand, (b) Dinuclear Cobalt(II) cryptate complex of ligand containing activated carbonate bridge.

**Synthesis of modified SiO$_2$ materials:** The synthesis of SBA-15 has been widely discussed, e.g. see [36] and its modification (with a range of organic functionalities including alkyl halide species), [37, 38] has also been previously described.

**Synthesis of SBA-15:** 4.4 g of triblock copolymer was dispersed in 30 g distilled water and stirred for 1.5 h. To this solution, 120 g of 2 M HCl was added and stirred for 2 h. 9.0 g of TEOS was added dropwise and the mixture was maintained at 45 °C for 24 h. The crystallized product was filtered, washed with distilled water and dried at 80 °C. It was then calcined at 450 °C for 8 h in air in order to remove the template material.
Synthesis of Cl modified SBA-15: 5g of calcined SBA-15 was suspended in 100 mL of toluene and 5 mL of 3-Chloro propyltriethoxysilane was added to the mixture. The reaction mixture was refluxed for 12 h with stirring at 80 °C. The modified SBA-15 was collected by filtration and dried. This material is denoted as SBA-15-Cl.

Tethering of the complexes to the modified SBA-15: In these preparations the cryptand ligands were tethered to the surface of the modified SiO₂, and the resultant solid was treated with a solution of a Co or Cu salt in order to populate the two metal ion sites within each macromolecule. The ligand (1.196 g) was dissolved in dry acetonitrile (150 mL) and set to reflux under an inert atmosphere. Potassium carbonate (0.553 g) was added to the solution. The mixture was allowed to reflux for 10 minutes before potassium iodide (0.664 g) was added and the solution allowed to reflux for a further 20 minutes. SBA-15-Cl (0.5 g) was then added. The solution was allowed to reflux for 72 hours before cooling to room temperature. It was then vacuum filtered and the solid (Ligand-SBA-15-Cl) washed with water and methanol and allowed to dry under vacuum for 30 minutes.

To saturate these materials with metal ions, 0.5 g of the tethered ligand – containing material was added to a solution of cobalt tetrafluoroborate (0.2 g) in ethanol and acetonitrile (in a 50:50 ratio) and stirred at room temperature for 2 hours. The solution was then filtered and washed with ethanol: acetonitrile 50:50 and allowed to dry. The resultant solid is denoted here as Co-SBA-15–Cl. The tethered crypt containing a pair of Cu (II) ions was prepared in a similar manner and is denoted as Cu-SBA-15–Cl. Figure 6 shows the steps involved in the preparation of the final material.
Material Characterization: The synthesized SBA-15, modified SBA-15 and the final catalysts are characterized by various techniques including XRD, SAXS, BET, FTIR and TGA. X-ray diffraction (XRD) patterns were measured using a Siemens diffractometer with Cu Kα radiation (Kα = 0.154 nm). BET surface area, pore-size distribution and pore volume were determined by N₂ physisorption (Quantachrome Nova 2200e). FTIR spectra were recorded with a Bruker Vertex 70 System equipped with an MCT detector. The spectral range from 4000 to 600 cm⁻¹ was investigated using 64 scans with a resolution of 2 cm⁻¹. Thermogravimetric Analysis (TGA) was conducted on a TA-Q500 instrument under a flow of air at a total flow of 100 mL min⁻¹. Approximately 10 mg of the sample was heated in a platinum crucible from 30 to 1000 °C at a heating rate of 10 °C min⁻¹. The changes in mass of the complex and the tethered complexes were monitored as a function of temperature.

Reaction conditions: The activity of these catalysts was tested for chemical fixation of CO₂ through reduction with H₂ in a Parr reactor. In each reaction, 0.25 g of
catalyst was suspended in 150 mL of cyclohexane and the reactor (total volume 300 mL) pressurized with 0.5 bar CO$_2$ and 1.2 bar H$_2$ with a total pressure of 45 bar in Ar. The reaction was carried out at temperatures of 150 °C and 200 °C for 4 h. Fresh samples of catalyst were used for each experiment. Liquid phase and gas phase samples were withdrawn and analyzed in two Gas Chromatographs (one calibrated for liquid phase analysis and one for gas phase analysis). The liquid phase samples were analyzed in a Shimazdu GC-14B using a HP-PLOT/U capillary column while the gas phase was analysed in a Varian GC-450 equipped with molecular sieve and Hasysep columns. Further analysis of the liquid phase was carried out using ion-chromatography in order to probe for the presence of formate, acetate and oxalate anions.

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**References**


Figure S1 Typical Small angle XRD profile for SBA-15 (□), SBA-15 functionalised with Cl (X), SBA 15 functionalised with the cryptand material (○) and SBA 15 functionalised with the cryptand material in the presence of Cu (△). Profiles are displaced for clarity.
Figure S2

Figure S2. Typical TEM images of SBA-15, Cl-SBA-15 and Cu-SBA-15-Cl.
Figure S3

Figure S3. FTIR spectra of Ligand-SBA-15-Cl, Co-SBA-15-Cl and Cu-SBA15-Cl.
Figure S4 DTGA of Cu(BF$_4$)$_2$·xH$_2$O
Figure S5. DTGA profiles of the tethered Co and Cu catalysts before and after use.