Short communication

Conversion of CO_2 to methanol over bifunctional basic-metallic catalysts

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ABSTRACT

Amine functionalized silica is an excellent sorbent for CO_2 and when combined with Pd it has been demonstrated to selectively hydrogenate chemisorbed CO_2 to methanol at a pressure of 1 bar H_2. Up to 25% of the irreversibly captured CO_2 could be converted by applying a dynamic switch between adsorption at 70 °C and conversion to methanol at 140 °C. The surface species, observed during sorption and reaction by IR spectroscopy, allowed to conclude that the reaction proceeds via formation of carbamates and their gradual reduction to methanol on sites located at the interface between the amine and Pd particles.

1. Introduction

Efficient carbon capture and utilization (CCU) is a key element for a sustainable, carbon neutral economy [1]. The current CO_2 separation technology using pressure swing adsorption as well as the dynamic availability of renewable energy requires the development of processes being able to operate during dynamic changes in the reactant concentrations [1,2]. The sorption of CO_2, followed by hydrogenation to methanol with green H_2 during a reactive regeneration is a novel concept to utilize CO_2 as carbon source for the production of bulk chemicals and fuel components. For being successful, dynamic operation at low temperatures and high selectivity to methanol are required to reach a sufficient methanol yield.

Over the last years, several studies were reported on the hydrogenation of amine bound CO_2 to methanol at temperatures below 150 °C and at H_2 partial pressures of 20–80 bar using molecular catalysts [3]. Rezayee et al. reported the combination of CO_2 capture by dimethylamine and its (stepwise) reduction to methanol using a molecular Ru-based catalyst [4]. Kothandaraman et al. applied this concept to CO_2 directly captured from air using the combination of a polyamine capturing agent and a Ru-MACHO complex as catalyst for subsequent hydrogenation [5]. Both studies use amines to bind CO_2 in combination with a molecular hydrogenation catalysts and show that the initially formed carbamate ($RNCOO^-$ NH_3^+) is converted to an amide in the first step [3]. Due to the stability of amides, a second step at higher temperatures (~150 °C) is necessary to reduce the amide to methanol. With respect to amine and catalyst degradation the approach of increasing the temperature between CO_2 sorption and reduction proved to be more

efficient compared to an operation at constant (elevated) temperature [3–5]. It should be mentioned that amines were not only used for thermal catalysis, but for photo- and electrocatalysis as well [6]. All studies suggest that the amines do not only serve as CO_2 binding site, but also enhance activity and selectivity by transition state stabilization [3,6]. As CO_2 hydrogenation to methanol competes with methane formation, the catalyst should bind CO_2 without breaking both C—O bonds.

Despite the remarkable advancements using homogeneous catalysis, the reported systems face the challenges of typically high H_2 pressures (20–200 bar), the complex product recovery, as well as catalyst recycling [7]. Thus, we aim at transferring the catalytic reaction to solid catalysts, applying the concept of the enhanced reactivity of amine bound CO_2 for the reduction to methanol. While not being the rate determining step, electron transfer to bind CO_2 appeared to be critical in the initial stage of CO_2 activation [8–11]. Amines have been shown to provide the required basicity (electron pair donor strength) and, thus a combination of CO_2 capture by chemisorption on amines and subsequent reduction of the chemisorbed species with H (supplied from a noble metal component) should be successful if both functionalities are in the close contact.

In the work presented, we study the reaction mechanism of the hydrogenation of CO_2 to methanol over a bifunctional (basic – metal) heterogeneous catalyst for the low temperature conversion to methanol at atmospheric pressure and aim at transferring the catalytic reaction from a reaction in the homogenous phase to a solid sorbent/catalyst (heterogeneous) system.
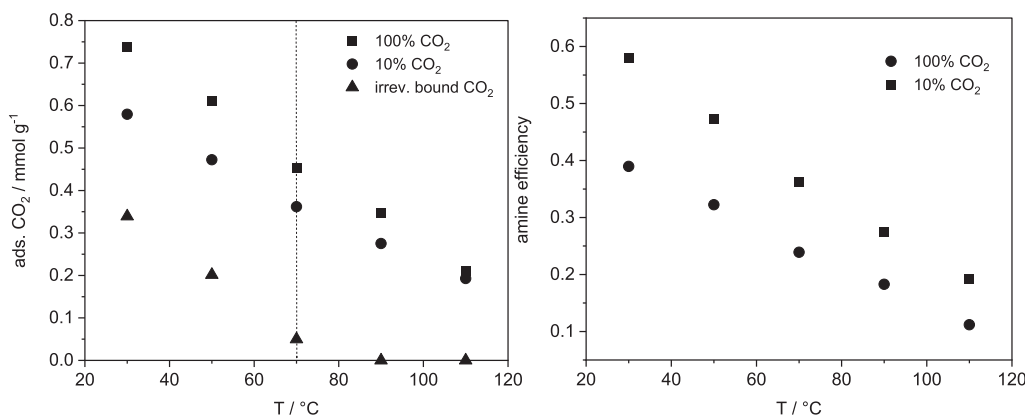
Fig. 1. (left) Adsorption isobars of PdAm1 at 100% CO_2 and 10% CO_2 (1 atm.). The triangles show the amount of irreversibly adsorbed CO_2 (after purging with N_2 at const. T). (right) Amine efficiency of PdAm1.
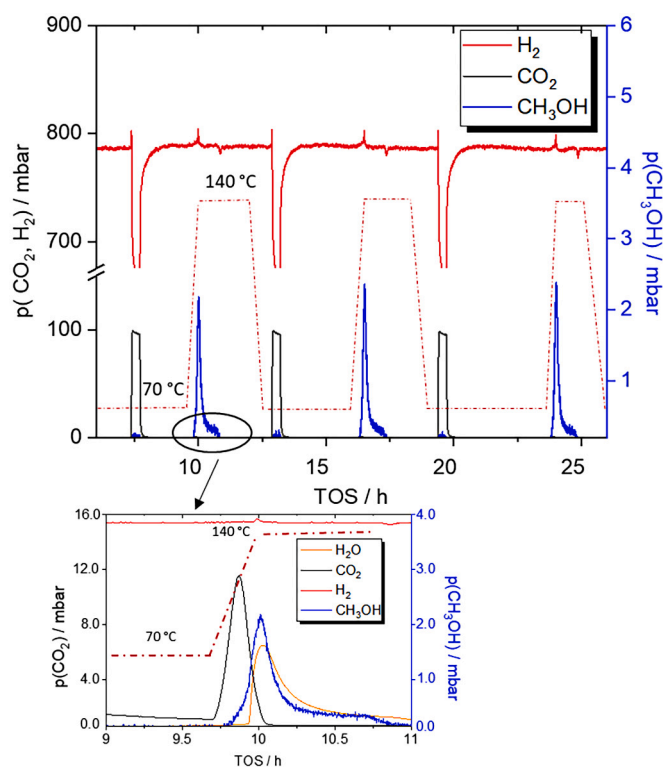
Fig. 2. Periodic adsorption and hydrogenation of CO_2, the catalyst was first loaded with CO_2 at 70 °C (100 mbar CO_2 in He), subsequently hydrogenation was carried out with H_2 (780 mbar in He) at 70 °C before increasing the temperature to 140 °C. The insert shows that unreacted CO_2 desorbs first, followed by methanol and water. Note, the scaling of the MS signals on the y-axis is different for reactants and products.

2. Experimental

The conditions of preparation, characterization and catalytic tests of the catalysts are described in detail in the Supporting Information (SI).
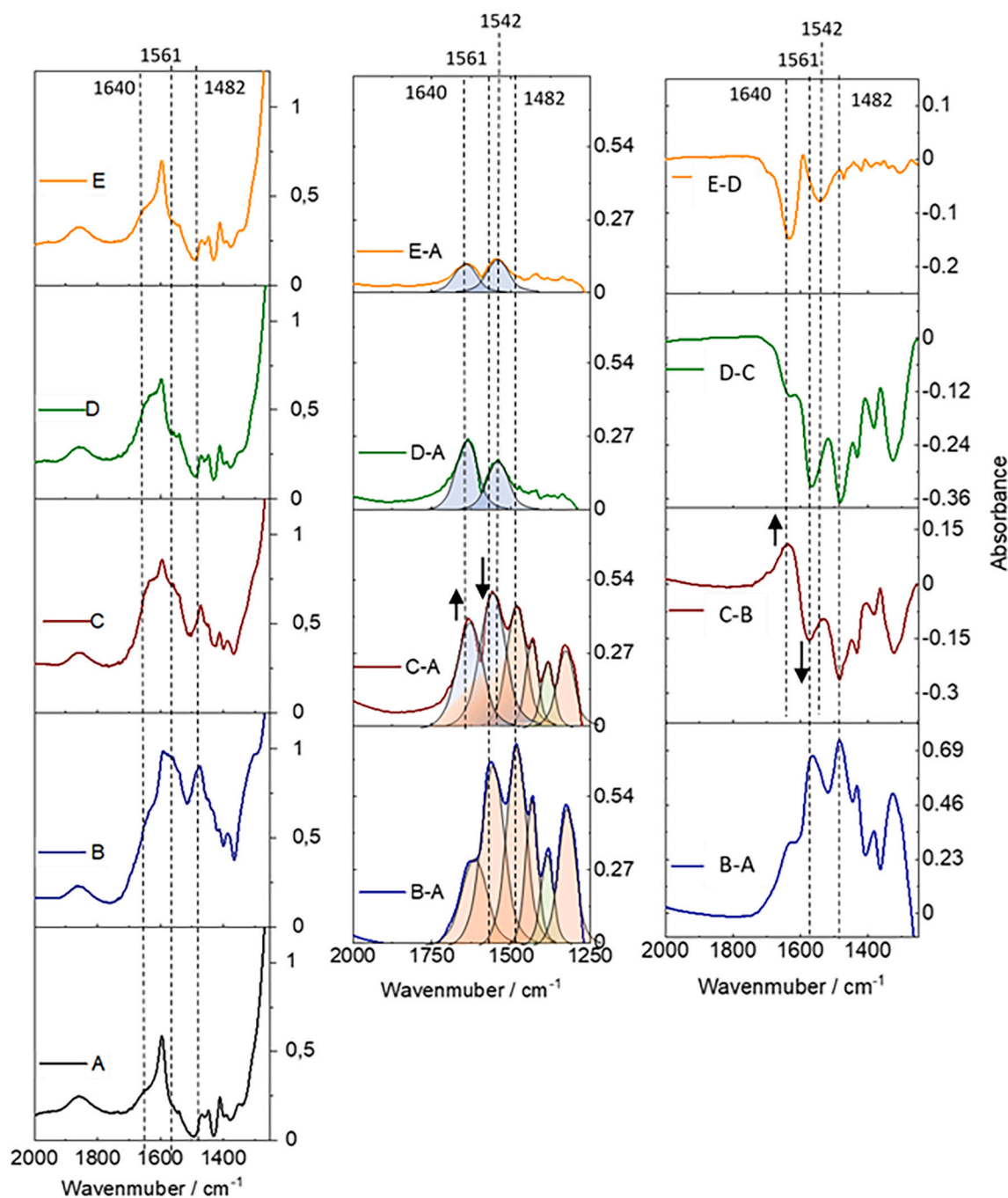
3. Results and discussion

3.1. Amine efficiency as function of temperature and CO_2 partial pressure

Adsorption isobars for the PdAm1 are shown in Fig. 1 on the left. The difference in CO_2 sorption capacity between pure (100%) and diluted (10%) CO_2 decreases with increasing temperature. A fraction of the CO_2 remains irreversibly adsorbed on the surface after switching from CO_2 to N_2, indicating that sorption sites with different strengths were present on the sorbent/catalyst. This is additionally supported by the significantly higher adsorption enthalpies observed at low coverage ($\Delta H_{ads} = -95$ kJ/mol) compared to higher coverage ($\Delta H_{ads} = -65$ kJ/mol) (Fig. S2), which agrees with values reported in literature [12]. The fraction of irreversibly adsorbed CO_2 decreases with temperature from 46% at 30 °C to 0% at 90 °C.

The dotted line in Fig. 1 indicates the conditions used for CO_2 adsorption in the experiments reported. The overall CO_2 uptake by the bifunctional PdAm1 at reaction conditions (70 °C, 100 mbar CO_2) was 0.45 mmol g^{-1} (0.24 mmol CO_2 mol^{-1} RNH$_2$) and 0.05 mmol CO_2 mol^{-1} RNH$_2$ were retained after purging at 70 °C (irreversibly adsorbed CO_2). Fig. 1 right shows the amine efficiency, i.e. number of CO_2 molecules adsorbed per –NH$_2$ group, as function of temperature at 100% and 10% CO_2 partial pressure (1 bar total pressure.). Note that binding of CO_2 as ammonium carbamate (HNCOO$^-$ NH$_3^+$) requires 2 amine groups in close distance [13,14], thus the maximum amine efficiency under dry conditions is 0.5.

3.2. Catalytic activity

The reaction was carried out by a periodic variation between sorption and reaction conditions. CO_2 was adsorbed at 70 °C until saturation

Table 1
Physicochemical properties and CO_2 conversion of the tested catalysts with constant amine loading and varying metal loading.

Sample	Conversion based on CO_2 irrev. ads. [%]	Conversion based on CO_2 total. ads. [%]	Amine [mmol g^{-1}]	Pd [wt %]	BET [m^2]	NH$_2$ density [nm^{-2}]	Pd particle diameter[a] [nm]
PdAm1	24.4	4.7	1.7	6.1	85	12.0	45
PdAm2	14.2	2.8	1.6	3.5	83	11.6	35
PdAm3	12.6	2.4	1.7	1.5	89	11.5	20
Pd_only	–	–	–	7	370	–	
Am_only	–	–	1.6	–	95	10.1	

[a] Diameter of unreduced particles.

Fig. 3. IR spectra (left) and corresponding difference spectra. The middle column shows the changes relative to the activated catalyst (spectrum A). The right column depicts the changes between each step. A: activated catalyst. B: After CO_2 adsorption. C: After 1 h reaction with 780 mbar H_2 at 70 °C. D: After 12 h flushing with N_2 at 140 °C. E: After 5 h reaction with 780 mbar H_2 at 140 °C. The arrows in the difference spectra of C should emphasize the increase of the band at 1640 cm^{-1} (amide) and the decrease of the band at 1561 cm^{-1} (carbamate) upon reaction with H_2. Bands originating from carbamate are colored orange, from carbamic acid green and from amide blue. Multicolor bands depict overlapping bands of the corresponding species. For the sake of clarity, only the most relevant bands are marked, detailed assignments can be found in the SI. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

was reached after about 10 min. Please note that saturation refers to the maximum uptake at the given conditions (100 mbar 70 °C), not to the maximum CO_2 uptake capacity of the material at lower temperature and higher partial pressure which is 0.74 mmol g^{-1} at 30 °C and 1 bar CO_2 partial pressure (see Fig. 1.). After equilibration with CO_2 the feed was switched to 780 mbar H_2 in He and initially kept at 70 °C for 90 min before increasing the temperature to 140 °C (Fig. 2). The purpose of the isothermal operation at 70 °C after CO_2 loading was to purge the system in order to avoid amine deactivation from reaction with CO_2 at higher

temperatures [15]. Upon heating to 140 °C up to 24% (0.01 CH$_3$OH mol mol^{-1} RNH$_2$) of the irreversibly adsorbed CO_2 (0.083 mmol g^{-1}) was converted with almost 100% selectivity to methanol and water. Other compounds with mass fragments from up to $m/z = 50$ (i.e., CO, CH$_4$, CH$_2$O, HCOOH, CH$_3$CH$_2$OH and amines) were not detected (for details see section E of the SI). Increasing the metal loading increases the concentration of active sites at the metal – amine interface, which resulted in an increase in the CO_2 conversion (see Table 1). PdAm2 and PdAm3 show similar conversion, since the increase in metal loading was
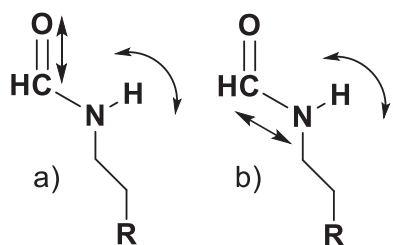
Scheme 1. Vibrational modes of amide I (a) and amide II band (b).

compensated by larger particle sizes, showing that the crucial parameter for achieving high activity is the concentration of sites at the perimeter between the metal and the amines. The formation of CO and CH_4 was not observed in experiments with the bifunctional catalyst. Catalysts loaded with amine (Am_only) or palladium only (Pd_only) as well as a physical mixture of both components (Pd_only + Am_only) did not exhibit any detectable conversion of CO_2, which confirms that the metal – amine interface in the bifunctional catalyst is essential for the methanol formation.

As already mentioned, it is well known that amines are prone to deactivation at high CO_2 partial pressure and temperatures above 100 °C by forming stable urea bridges [15], therefore we expected a decreased activity after a few cycles. However, after 10 cycles the material showed no measurable loss of activity or change in selectivity, which indicates that the CO_2 partial pressure during the phase of elevated temperature is too low to cause significant deactivation.

3.3. IR spectroscopy under reaction conditions

IR spectroscopy was used to analyze the surface species during CO_2 adsorption and the subsequent hydrogenation to methanol. The IR spectra during the different stages in the reaction cycle are shown in Fig. 3.

Spectrum B (Fig. 3) was recorded after exposing the catalyst to 10% CO_2 in He at 70 °C for one hour followed by flushing with N_2 for 30 min in order to remove weakly adsorbed CO_2. The formation of bands at 1630, 1561, 1482, 1430, and 1380 cm^{-1} was observed, which resulted from the formation of carbamic acid and carbamates upon sorption and reaction of CO_2 on the primary amine groups [16]. The detailed band assignments can be found in Table S1 to S3. Spectrum C was collected after H_2 (78% in He) was flown over the sample at 70 °C for one hour. The decrease in intensity of the bands associated with the presence of carbamate/carbamic acid (1561 and 1482 cm^{-1}) was accompanied by the appearance of a band at 1640 cm^{-1} and a shoulder at 1542 cm^{-1}, attributed to the presence of amides (amide I and amide II bands) [17]. The broad band around 3320 cm^{-1} can be attributed to the hydrogen bonded N—H stretching vibration of the amide (vibrational modes shown in Scheme 1 and corresponding IR spectra shown in Fig. 4 and Fig. S5) [17,18].

After 12 h flushing with N_2 at 140 °C. E: After 5 h reaction with 780 mbar H_2 at 140 °C. For the sake of clarity, only the most relevant bands are marked, detailed assignments can be found in the SI.

The intensity of the (negative) bands of the C—H stretching vibration of the -CH$_2$- groups remained almost constant, although the carbamate concentration on the surface decreased. This indicates that the amide has the same effect on the electronic structure of nitrogen as the carbamate, since both molecules contain a carbonyl group. The nitrogen of the amine has a free electron pair and donates electron density into the σ^*_{C-H} orbital of the -CH$_2$- group of the propyl group, next to the nitrogen. This interaction leads to a weakening of the C – H bond and results in an increase in the intensities of the corresponding C – H stretching vibrations [19]. After the carbamate/carbamic acid is formed, the electron donation is suppressed by the formation of a carbonyl-group, resulting in decreased intensities and, therefore, negative bands

were observed in the difference spectra.

As the bands of unreacted carbamate, carbamic acid and amides are strongly overlapping at lower wavenumbers, the catalyst was flushed with N_2 for 12 h at 140 °C to desorb unreacted CO_2 and water, formed by carbamate hydrogenation. After this step, bands assigned to carbamate/carbamic acid were not observed (Spectrum D), while bands characteristic of the amide at 3300 cm^{-1}, 1640 cm^{-1} and 1542 cm^{-1} were still present. The corresponding difference spectrum in the right column (Spectrum "D-C") shows the decrease of bands associated with chemisorbed CO_2. Note that a negative band at 1630 cm^{-1} was observed, which is tentatively attributed either to the removal of NH_3^+ species (carbamate) and/or to the desorption of water. Subsequently, the temperature was increased to 140 °C in 78% H_2 in He at 140 °C in H_2 flow and kept at this temperature for 5 h. During the reaction at elevated temperature, the amide bands decreased (spectrum E and "*E*-D"), confirming the hydrogenation to methanol and subsequent desorption of the product.

To confirm the band assignments to the amide intermediate, a sample with the amide grafted on the surface (instead of the amine) was used. The sample was exposed to 10 mbar H_2 at 70–160 °C and the decrease of the amide I (1660 cm^{-1}) and amide II (1535 cm^{-1}) band at 160 °C was accompanied by an increase of a band at 1592 cm^{-1}, which is assigned to the R-NH$_2$ - deformation band of a primary amine (Fig. S6). This experiment is a direct proof that amides are stable surface intermediates, which subsequently undergo hydrogenolysis to methanol and the primary amine. However, only a fraction of the grafted amide was converted, which further supports the hypothesis that only species in direct proximity to the Pd-particle can be reduced.

Please note that the location as well as the relative intensity of the amide I and II band are highly sensitive to the chemical environment. The stronger the H-bonding the lower frequency of the amide I band (1640 cm^{-1}) and the higher the frequency for the amide II band (1542 cm^{-1}) [17], indicate that the amide formed during the reaction (Fig. 3) forms relatively strong H-bonds to neighboring species (amine, amide, silanol).

3.4. Catalytic cycle

Based on the surface species detected by IR spectroscopy and recent theoretical and experimental studies on homogeneous metal – amine systems for CO_2 hydrogenation [5,20,21] we would like to propose the following reaction mechanism for the conversion of CO_2 to methanol (Scheme 2).

In the first step CO_2 is adsorbed on the amine group forming a carbamate. In order to form and stabilize the ionic carbamate, two amine groups in close proximity are required, although CO_2 can also adsorb on one amine as a zwitterion, which is, however, less stable [13]. Earlier studies showed that a higher amine density resulted in a higher stability of adsorbed CO_2, presumably through hydrogen – bonding with neighboring amines [12,22–24]. In the next step, the carbamate is reduced to the amide by H already at 70 °C, releasing one molecule of water. This step proceeds conceptually by the substitution of the acid OH group by a hydride in parallel to the proton addition to the leaving OH group. Assuming a homolytic dissociation of H_2, it is hypothesized that the generation of the hydrogen species requires the Pd-support interface. The stability of the amides requires to increase the temperature to 140 °C for the reduction via a hemiaminal intermediate [20]. This latter reduction step may proceed via two alternative pathways by cleaving the C—N bond leading to methanol (desired) or by cleaving the C—O bond leading to water and a secondary amine (undesired), which is difficult to remove from the product stream and would lead to an irreversible loss of the functional (amine) groups on the sorbent/catalyst being essential for the CO_2 sorption..

It should be noted that although hydrogenation of amides was subject to many studies, only few solid materials were able to reduce amides selectively via C—N cleavage [25–28], which we solely observed as IR
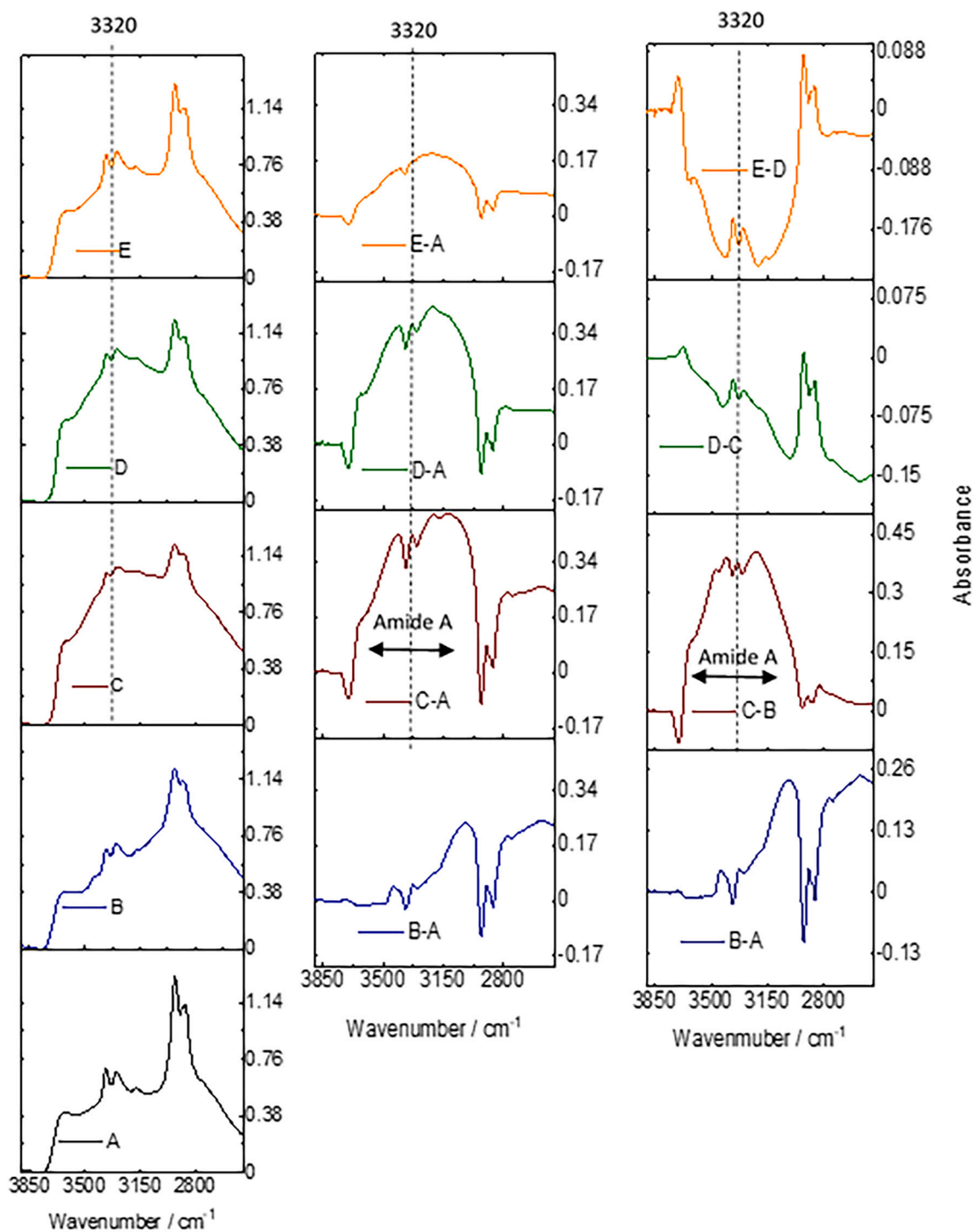
Fig. 4. IR spectra (left) and corresponding difference spectra. The middle column shows the changes relative to the activated catalyst (spectrum A left). The right column depicts the changes between each step. A: activated catalyst. B: After CO_2 adsorption. C: After 1 h reaction with 780 mbar H_2 at 70 °C. D:

spectra taken from the catalyst after several cycles confirmed the absence of methylated amines (Fig. S3). Recent theoretical and experimental studies on homogeneous systems suggest a cooperative effect of basic nitrogen species (amides, amines) favoring the C—N cleavage [20,21]. This cooperative effect results from the N—H moiety acting as proton shuttle, transferring the proton from the O to the N end of the hemiaminal, thus, inducing the C – N cleavage [20,21].

4. Conclusions

We report a heterogeneous, amine assisted sorbent and catalyst for CO_2 hydrogenation that combines gas phase CO_2 capture and hydrogenation on the same site. Conversions of up to 25% of the irreversibly adsorbed CO_2 were achieved at mild conditions (1 bar, 70–140 °C), with a high selectivity towards methanol. IR spectra under reaction conditions showed that the catalytic cycle proceeds via amide and hemiaminal species. The amine species present in the bifunctional catalyst have a dual functionality in the reaction. They acts as adsorption site for
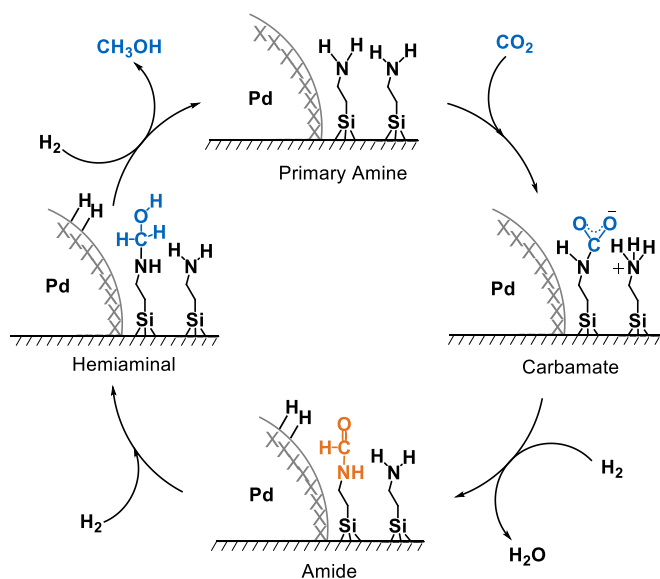
Scheme 2. Proposed mechanism of carbamate hydrogenation via formamide and hemiaminal intermediates

CO_2, but also direct the selectivity towards C – N cleavage during the hydrogenation of the amide by acting as proton shuttle or by transition state stabilization. Therefore, the dual functionality of base and metal groups at the amine/Pd interface is essential for an active sorbent/ catalyst for the direct hydrogenation of CO_2 with a high yield to methanol.

Author statement

JP and EB performed the experiments and analyzed the data. JAL and AJ conceived the experiments, analyzed the data and wrote the manuscript with significant input from all co-authors.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.catcom.2021.106347.

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