

Chemical Utilisation of CO₂

A Challenge for the Sustainable World

Dinesh Jagadeesan, Bhaskar Joshi, Prashant Parameswaran

We derive more than 80% of our energy and chemicals from fossil fuels such as oil, coal and natural gas. Depleting resources and environmental pollution are forcing us to look for alternative resources. Carbon dioxide (CO₂), which is produced in large quantities, could be recycled to chemical feedstocks.

Carbon Crisis – Need for Alternative Technologies

Carbon is a ubiquitous element that drives the modern economy. For the last several decades, we have been depending upon carbon-rich fossils such as coal, oil and natural gas to produce energy and chemical feedstocks [1]. Fossils are either used directly or processed to form fuels, additives, lubricants and a variety of raw materials to produce drugs, plastics, fertilizers and other essential products [2]. *Table 1* summarizes some of the products that are obtained from fossils and their end uses.

The continuous usage of fossils for the production of fuels and chemical feedstocks has led to two major problems. First, fossils are non-renewable and cannot be replenished within the human timescale. World's total of proven coal reserves is only 909,000 Mt and that of oil reserves is 1,189 billion barrels (estimated in 2005) [3]. At the present rate of consumption, fossils may be used up in less than a 100 years. Due to rising demands, it is unlikely that any of the alternate resources such as hydro, geo, wind, solar or nuclear will entirely replace fossils [4–7]. Even if we develop an efficient alternate energy technology in the future, our primary dependence on fossils to produce chemical feedstocks will remain unabated. We are, therefore, facing a carbon crisis with respect to the non-availability of hydrocarbon resources to produce chemical feedstocks. Another concern is that the incessant



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Keywords

Chemical recycling, CO₂ conversion, catalysis, sustainability.



Feedstock	Industrial uses
Caprolactum and hexamethylenediamine	Nylon
Vinyl chloride	Polymer
Styrene	Tyres and foams for packing materials
Formaldehyde	Resins for electrical appliances
H ₂ SO ₄	Industrial catalyst
Benzene	Dyes
Olefins	Monomers and polymers
Toluene	Varnishes and adhesives
Phenols	Pharmaceuticals

Table 1. Some refinery products and their end use in the industry.

exploitation of fossil resources (or fossil-derived products) produces large quantities of CO₂, polluting our environment. The increase in CO₂ level is so alarming that we must find a source of carbon which is a non-fossil, renewable, reliable, sustainable and non-polluting.

Importance of Recycling CO₂

Some of the causes of rising atmospheric CO₂ levels are increasing population, land use, forest fires, volcanic eruptions, deforestation, automobile combustion, power generation, iron and steel

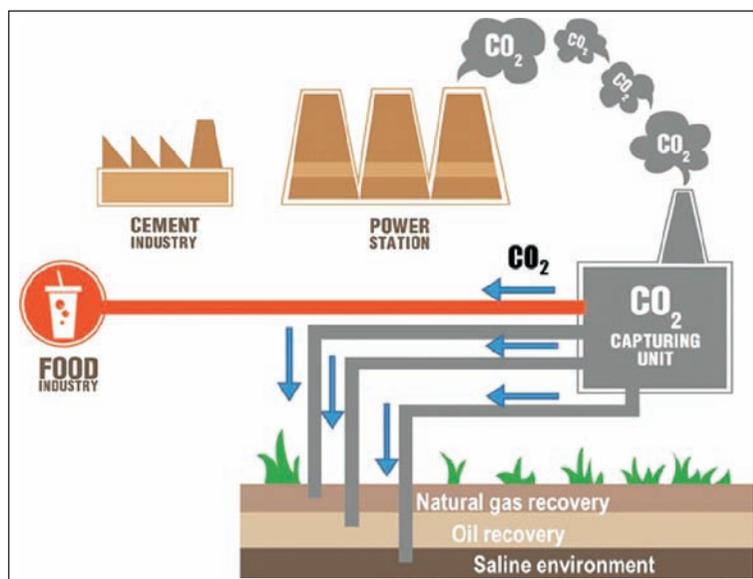


Figure 1. Major sources of CO₂ production and utilisation units.



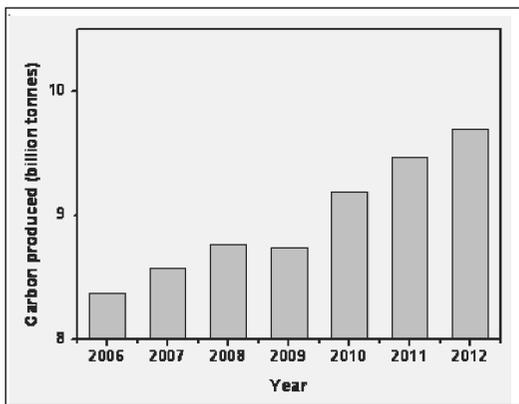


Figure 2. Global production of carbon produced in the form of CO₂.

production and cement production (*Figure 1*). In the recent decade, many research efforts were directed to the physical capture and storage of CO₂ at the site of production. Instead of capturing and storing large volumes of atmospheric CO₂, it may be useful to chemically convert CO₂ back into H-rich hydrocarbons for fuel or feedstock applications. *Figure 2* shows the weight of carbon produced globally in the form of CO₂. Even if we recycle 10% of the total carbon emitted, we can meet substantial demands for feedstock¹ chemicals. Recycling CO₂ is, thus, a promising route to tackle both, the carbon-crisis and the environmental pollution. Abundance and non-toxicity of CO₂ also make recycling very attractive.

Despite research efforts to chemically recycle CO₂ since the 1970's, the problem has remained as one of the important synthetic challenges in modern chemistry. So far, there are only four industrial processes that chemically utilize CO₂ [8].

- Production of urea (105 million tons) by reacting with NH₃ to produce fertilizers.
- Production of salicylic acid (90,000 tpa) by the Kolbe–Schmitt process by reacting CO₂ and sodium phenolate for the production of aspirin.
- Production of cyclic organic carbonates (80,000 tpa) by reacting CO₂ with epoxides for the manufacture of plastics.
- Water–gas shift reaction in the methanol synthesis.

¹ Feedstocks are those set of chemicals which can be used as an important starting material in chemical industries to produce other chemicals necessary for the production of chemicals such as monomers, dyes, pharmaceuticals and plastics.

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The limited utilization of CO_2 as a building block not only points out the intrinsic challenges associated with the reactions but also highlights tremendous opportunities to overcome the challenges and expand the scope of chemical utilization of CO_2 .

Promising Reactions for CO_2 Utilisation

Aresta *et al* [9] broadly classified the CO_2 -utilizing reactions in two categories. The first category involves reactions where the native oxidation state of carbon in CO_2 (+4) is retained. Such reactions mainly involve incorporation of CO_2 in a chemical bond to form esters, carbamates, carboxylic acids, carbonates, urea and polymers. They require less input of energy and can be carried out under milder conditions. Besides, most of the products formed under this category can be used as feedstock chemicals. In another category of reactions, the oxidation state of CO_2 is reduced by at least two units. These are energy-consuming processes and energy is provided in the form of electrons, photons or hydrogen. The products formed under this category are hydrocarbons, CH_4 , CO , CH_3OH , HCOOH , etc., most of which have fuel applications.

Gomes *et al* [10] have graphically plotted various directions that can be adopted to develop alternatives to petrochemical products by recycling CO_2 . An important type of reaction is the insertion of CO_2 into an organic chain. These reactions usually involve the C–N and C–O bond formation without adding any H atoms at the carbon center. They are also termed as chemical functionalization and are used in the synthesis of new materials. Gomes *et al* also suggested a diagonal approach, where both functionalization and reduction must be carried out to produce more variety of products.

Indirect utilization of CO_2 is also gaining importance [12]. For instance, CO_2 is naturally sequestered as alkaline metal carbonates (e.g., calcite) in many parts of the world. They occur abundantly and unlike coal or oil are not limited by their geographical locations. It takes a few hundred years for CO_2 to get converted to

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calcite (CaCO_3). This process can be accelerated to a few hours by various technologies. One of the proposals is to use calcite as the source of carbon. It has been shown that calcite can decompose in the presence of H_2 to form many types of hydrocarbons. This reaction is catalyzed by many transition metals. This process may become a viable route to synthetic fuels if the conversion and selectivity of the reactions are improved [13,14].

Challenges in Recycling CO_2

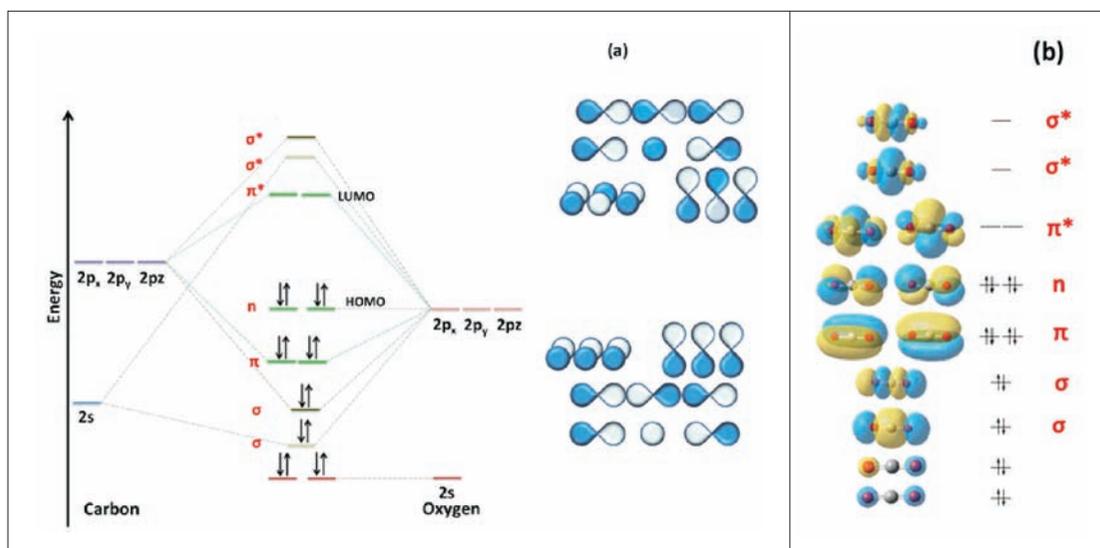
CO_2 is thermodynamically a very stable molecule with a free energy of formation², $\Delta G_f = -390 \text{ kJmol}^{-1}$, which is lower than that of most of the possible products. This makes the chemical conversion thermodynamically an uphill process [15]. The exceptional chemical stability of CO_2 is evident from the unusually strong C=O bonds. The C=O bond distance is around 1.16 \AA in CO_2 , while it is 1.23 \AA in acetic acid. A substantial input of energy is needed for the CO_2 to react. This is usually reflected as a high activation energy in CO_2 conversion. A catalyst capable of weakening the C=O bonds by specific chemical interactions is essential to reduce the activation energy of the CO_2 conversion. In order to activate CO_2 , electrons are added to the HOMO π^* , which eventually increases the electron density on the carbon

² The energy level of a molecule is determined by the extent of free energy change that occurs during the formation of one mole of the product molecule from the corresponding elements all in their standard states.

Figure 3. (a) Qualitative representation of the molecular orbital diagram of CO_2 . (b) Graphical representation of the shape, symmetry and localization of the molecular orbitals.

Source:

<https://people.ok.ubc.ca/wsmcneil/220/MO-CO2-SF6-TM.pdf>

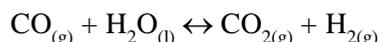


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atoms relative to the electron density shared between carbon and oxygen atoms (*Figure 3*). Therefore, the C=O bonds get weakened and the molecule becomes susceptible to reaction.

Catalysts for CO₂ Conversion

Transition metals, especially the 3rd row, are favorite candidates for catalyst research for CO₂ conversion. Motivation in this field began when it was realized that transition metals could enhance the production of H₂ in the water–gas shift reaction which is given below. This reaction is important because H₂ is one of the cleanest fuels and is an important raw material in a number of chemical industries.



Systematic studies of transition metal–CO₂ complexes revealed that coordination with transition metal ions can activate a CO₂ molecule and make it much more reactive than its native form. Transition metals which can undergo acid–base reactions involving *d*-orbitals are suitable to activate CO₂. Reactivity of CO₂ stems from the difference in the electronegativity between carbon and oxygen atoms. The carbon atom, which is highly electron-deficient, is Lewis acidic in nature and electron-rich oxygen atoms are Lewis basic. The first important step in the catalysis of CO₂ conversion is the binding of CO₂ to the transition metal. There are three basic types of interactions possible between CO₂ and the transition metals as illustrated in *Figure 4*.

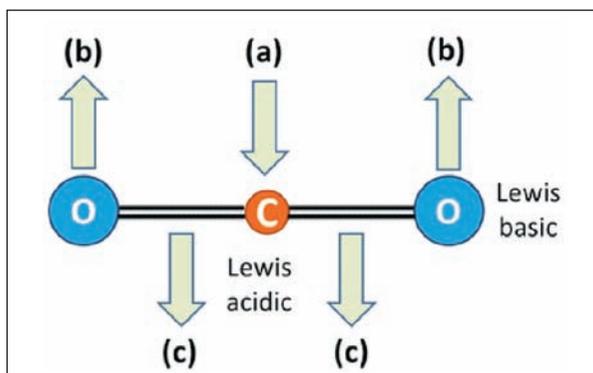


Figure 4. Different sites of reaction in a CO₂ molecule.

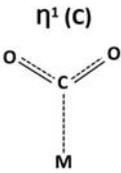
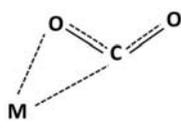
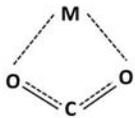


- a) *Reaction via carbon atom:* Anti-bonding π^* -orbital localized on the carbon atom has a tremendous role in the activation of CO_2 . Transfer of electrons to the carbon atom will convert CO_2 to a bent radical anion CO_2^- with a bond angle of 134° .
- b) *Reaction via oxygen atom:* CO_2 can transfer the non-bonding electrons on oxygen to an electrophilic species. However, an increased s character in sp^2 hybridized oxygen orbitals makes it relatively less basic compared to other compounds, such as H_2O . Its reaction towards Brønsted and Lewis acids is therefore, weak. This type of interaction with the transition metal does not activate CO_2 and is not significant in CO_2 conversion.
- c) *Reaction via π -bond:* CO_2 has two orthogonal π -bonds which can interact with d orbitals of the transition metals to form complexes.

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Only bonding modes which transfer electrons to the π^* -orbital of CO_2 and those which can stabilize the resultant radical anion CO_2^- have relevance to the activation of CO_2 [14]. In *Table 2*, three important modes of bonding between CO_2 and a single

Table 2. Coordination modes of CO_2 with single metal centers that are relevant to activation.

 <p style="text-align: center;">$\eta^1(\text{C})$</p>	Strong electron transfer occurs between d_z^2 -orbital of the metal and π^* -orbital of CO_2	Electron-rich transition metals in low oxidation states
 <p style="text-align: center;">$\eta^2(\text{C,O})$</p>	Sigma overlap between p-orbital of CO_2 to empty d_z^2 -orbital of metal. Back bonding occurs between filled d_{xy} -orbital of metal and empty π^* -orbital of CO_2	Electron-rich transition metals in low oxidation states
 <p style="text-align: center;">$\eta^2(\text{O,O})$</p>	Metal carboxylate with ionic M^+CO_2^-	Observed in alkali metals.



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metal center are presented. The first type is $\eta^1(\text{C})$, which is an important type of coordination, involving transfer of electrons from metal *d*-orbital directly to LUMO of CO₂. This activates the CO₂ molecule, which can be confirmed using IR spectroscopy by a red shift in the C=O bonds. The first complex synthesized by this type of coordination was Rh(diars)₂Cl(CO₂), where C=O bond lengths increased to 1.20 and 1.25 Å and bond angle changed to 126° [15]. In the second type of bonding mode, $\eta^2(\text{C,O})$, there is a double bonding. It is a side-on overlap of the π bond of C=O and the empty *d*-orbital of the metal. Transfer of electrons occurs from the CO₂ molecule to the metal with a back donation from metal to the ligand, as well. This type of interaction increases the strength of the M–C bond and weakens the CO bonds. Both $\eta^1(\text{C})$, and $\eta^2(\text{C,O})$ modes need electron-rich metals in low oxidation states (typically 0, +1 or +2). The third type of bonding is usually found in surface carbonates when alkali or alkaline metals react with CO₂. A classic demonstration of acid-base activation of CO₂ is when CO₂ acts as a bridging molecule between a sterically hindered Lewis acid and Lewis base ligands. D Stephan *et al* pioneered this concept of frustrated Lewis pairs¹ and used it to further convert CO₂ to CH₃OH [16].

¹ Pakkirisamy Thilagar and Sanjoy Mukherjee, *Frustrated Lewis Pairs, Resonance*, Vol.20, No.11, pp.1017–1027, 2014.

CO₂ coordinated to a metal can undergo rearrangements to form products. Mascetti *et al* used FT-IR spectroscopic techniques at low temperatures to study the complexes of CO₂ with 3rd transition metals. CO₂ was found to be in a bent shape in complexes with all the metals and the bond lengths slightly increased. However, according to the studies, the early transition metals (Ti, V and Cr), which have oxophilic character, readily inserted themselves into the CO bond of CO₂ to form thermally unstable O–M–CO or O–M–(CO)(CO₂) species. These complexes were very unstable and therefore had less usefulness in CO₂ catalysis. Among the late transition metals, Fe and Co were observed to form $\eta^1(\text{C})$ type of bonding. These complexes decomposed to form CO. Interestingly, Fe and Co are potential candidates in many CO₂ reduction reactions which can be ascribed to their ability to form stable $\eta^1(\text{C})$ bonding. An interesting example is



$\text{Ni}(\text{PH}_3)_2$ which prefers $\eta^2(\text{C},\text{O})$ coordination, while $\text{Ni}(\text{NH}_3)_4\text{F}$ prefers $\eta^1(\text{C})$ coordination. The reason is ascribed to the increased nucleophilicity of Ni in the latter complex.

A suitable reactant molecule in the vicinity of the activated CO_2 ligand as an external reactant or another ligand attached to the same transition metal is necessary to attack at the site of CO_2 coordination. This increases the probability of conversion of CO_2 to a desired molecule. For example, binding of CO_2 as in $\eta^1(\text{C})$ or $\eta^2(\text{C},\text{O})$ coordination creates excess charge localized on the oxygen atoms which are prone to electrophilic reactions with protons or epoxides. A number of Cu and Mn complexes which bind CO_2 in $\eta^1(\text{C})$ mode have been known to react with the epoxides at the less hindered carbon site forming cyclic carbonates [17].

CO_2 can also get activated by reacting with one of the ligands, usually the hydride, attached to the metal. This is followed by an insertion reaction of CO_2 into the M–L bond of a complex forming formate. Olefins are known to undergo oxidative coupling reactions with CO_2 in the presence of transition metals to form acrylates. A simultaneous binding of CO_2 and electrophilic reactions of oxygen can also occur. In this case, carbon is bonded to the metal center and oxygen of CO_2 reacts with one of the electrophilic ligands of the metal almost simultaneously. This pathway of combined acid–base activation is commonly observed in many reactions leading to products (Figure 5). Therefore, the catalyst to be designed must possess both nucleophilic (base) and electrophilic (acidic) centers. Presence of a highly reactive co-reactant will favor the thermodynamics of the reaction. A range of enzymes in plants, such as RuBisCO, carboxylases and carbonic anhydrases are active in chemically converting CO_2 to energy-rich molecules. Interestingly, not all enzymes in

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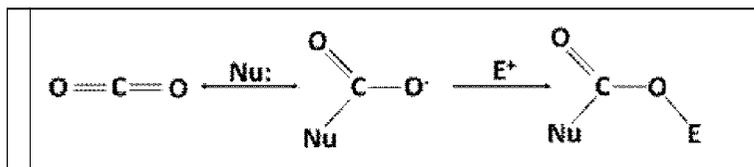


Figure 5. Simultaneous acid and base activation of CO_2 .



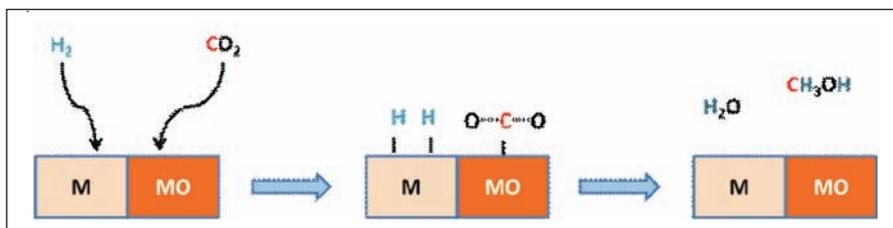


Figure 6. A strategy in heterogeneous catalysis involving dissociative chemisorption of CO_2 and H_2 facilitates the chemical conversion.

Nature use transition metals to activate CO_2 . Sometimes, transition metals in high oxidation states are used by Nature. Certainly the role of transition metals may be different in natural systems compared to the man-made complexes. The interplay of enzymes, pH and other factors makes the enzymatic chemistry mild, complex and efficient. For reactions such as the hydration of CO_2 , efforts to study enzyme chemistry and replicate to activate and convert CO_2 are being actively pursued [18].

Although a number of homogeneous catalysts have been developed and studied, there are inherent disadvantages such as the cost of preparation, sensitivity and poor recoverability. Heterogeneous catalysts win over these aspects. Although, they are not as efficient as homogeneous catalysts, they are more suitable for industrial scale reactions. Current challenges in the materials science are to develop heterogeneous catalysts for some of the potential CO_2 -utilizing reactions.

Opportunities

Design, synthesis and testing of catalysts make up an evergreen strategy that is commonly applied to the problem of CO_2 utilization. However, new challenges in this area of research are to translate the knowledge obtained in the homogeneous catalysis to the design and development of efficient heterogeneous catalysts and new reactions. Chemical synthesis, surface science and process engineering are the highest potential fields that can make substantial advancement in this field of research. There are at least a dozen reactions using CO_2 that have huge market potential. It is only a matter of time and concerted efforts by scientists across various disciplines to succeed in the endeavor to create

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useful materials out of thin air as a step towards a safe, green and prosperous planet.

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Suggested Reading

- [1] World Energy Council (WEC), <http://worldenergy.org/wec-geis/>.
- [2] B K B Rao, *Modern Petroleum Refining Processes*, Oxford & IBH Publishing Company Private Limited, 5th Edition, 2009.
- [3] G A Olah, A Geoppert and G K S Prakash, *Beyond Oil and Gas: The Methanol Economy*, Wiley-VCH, Weinheim, 2006.
- [4] Sheela K Ramasesha, Challenges in the quest for clean energies – background, *Resonance*, Vol.18, No.3, pp.206–217, 2013.
- [5] Sheela K Ramasesha, Challenges in the quest for clean energies – solar energy technologies, *Resonance*, Vol.18, No.5, pp.440–457, 2013.
- [6] Sheela K Ramasesha, Challenges in the quest for clean energies – wind technologies, *Resonance*, Vol.18, No.18, pp.756–770, 2013.
- [7] A L Donne, A Scaccabarozzi, S Tombolato, S Marchionna, P Garattini, B Vodopivec, M Acciarri and S Binetti, State of the art and perspectives of inorganic photovoltaics, *ISRN Renewable Energy*, Vol. 2013, <http://dx.doi.org/10.1155/2013/830731>, 2013.
- [8] H J Freund and M W Roberts, Surface chemistry of carbon dioxide, *Surface Science Reports*, Vol.25, pp.225–273, 1996.
- [9] M Aresta, A Dibenedetto and A Angelini, The changing paradigm in CO₂ utilization, *J. CO₂ Utilization*, Vol.3–4, pp.65–73, 2013.
- [10] a) C D Ne Gomes, O Jacquet, C Villiers, P Thuery, M Ephritikhine and T Cantat, *Angew. Chem. Int. Ed.*, Vol.51, pp.187–190, 2012. b) Eds. B M Bhanage and M Arai, Transformation and Utilization of CO₂, Green Chemistry and Sustainable Technology, DOI 10.1007/978-3-642-44988-8_3, Springer-Verlag Berlin Heidelberg 2014.
- [11] D Jagadeesan, M Eswaramoorthy and C N R Rao, *Chem. Sus.Chem.*, Vol.2, pp.878–882, 2009.
- [12] D Jagadeesan, Y Sundarayya, G Madras and C N R Rao, *RSC Adv.*, Vol.3, pp.7224–7229, 2013.
- [13] J De Paula and P Atkins, *Physical Chemistry*, 9th Edition, Oxford University Press, 2011.

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- [14] W Leitner, The coordination chemistry of carbon dioxide and its relevance for catalysis: a critical survey, *Coordination Chemistry Reviews*, Vol.153, pp.257–284, 1996.
- [15] J Mascetti and M Tranquille, Fourier transform infrared studies of atomic Ti, V, Cr, Fe, Co, Ni, and Cu Reactions with carbon dioxide in low-temperature matrices, *J. Phys. Chem.*, Vol.92, No.8, pp.2177–2184, 1988.
- [16] G Menard and D W Stephan, Room temperature conversion of CO₂ to CH₃OH using Al-based frustrated Lewis pairs and ammonia borane, *J. Amer. Chem. Soc.*, Vol.132, pp. 1796–1797, 2010.
- [17] R Srivastava, T H Bennur and D Srinivas, Factors affecting activation and utilization of carbon dioxide in cyclic carbonates synthesis over Cu and Mn peraza macrocyclic complexes, *J. of Mol. Cat. A – Chemistry*, Vol.226, No.2, pp.199–205, 2005.
- [18] S Schenk, J Notni, U Kohn, K Wermann and E Anders, Carbon dioxide and related heterocumulenes at zinc and lithium cations: bioinspired reactions and principles, *Dalton Transactions*, pp.4191–4206, 2006.
- [19] *Carbon dioxide as Chemical Feedstock*, Ed. M Aresta, Wiley –VCH Verlag GmbH 7 Co, 2010, ISBN 978-3-527-32475-0.
- [20] M Mikkelsen, M Jørgensen and F C Krebs, The teraton challenge. A review of fixation and transformation of carbon dioxide, *Energy and Environmental Science*, Vol.3, pp.43–81, 2010.

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