

Editorial

# CO<sub>2</sub> Valorization and Its Subsequent Valorization

Juan Antonio Cecilia <sup>1,\*</sup>, Daniel Ballesteros Plata <sup>1</sup> and Enrique Vilarrasa García <sup>2</sup>

<sup>1</sup> Department of Inorganic Chemistry, Crystallography and Mineralogy, Campus de Teatinos, Universidad de Málaga, 29071 Málaga, Spain; daniel.ballesteros@uma.es

<sup>2</sup> Grupo de Pesquisa em Separações por Adsorção, Department of Chemical Engineering, Campus do Pici, Universidade Federal do Ceará, Fortaleza C 60455760, Brazil; enrique@gpsa.ufc.br

\* Correspondence: jacecilia@uma.es

After the industrial revolution, the increase in the world population and the consumption of fossil fuels has led to an increase in anthropogenic CO<sub>2</sub> emissions. These emissions are directly related to a progressive increase in the temperature on the surface of Earth causing global warming, which is seriously affecting the environment and the living beings of the planet. The Intergovernmental Panel on Climate Change (IPCC) has published several reports which indicate the effects of global warming as well as the importance of minimizing anthropogenic CO<sub>2</sub> emissions to prevent more severe damage on Earth in order to achieve a cycle of zero-CO<sub>2</sub> emissions in the year 2050 [1]. Considering the severe effects of global warming, both governments and many scientists are making efforts to develop various strategies to reduce CO<sub>2</sub> emissions into the atmosphere.

Nowadays, various energy sources have been proposed to replace traditional fossil fuels. However, energy demands are so high that it is impossible to substitute fossil fuels in the short term. Considering these premises, the most mature strategy is focused on the design of more efficient processes where CO<sub>2</sub> emissions can be minimized and, on the other hand, CO<sub>2</sub> sequestration and its subsequent valorization to obtain high added value chemicals.

The task of reducing CO<sub>2</sub> emissions is very complex, but at the same time very exciting, since more efficient processes and technologies to capture CO<sub>2</sub> require offsetting emissions between 100 and 1000 Gt throughout this century [1].

This special issue is focused on highlighting new approaches to capturing CO<sub>2</sub> from industrial sources such as electricity-generated power, refineries, steel or cement among others, as well as from the ambient air [2]. Once the CO<sub>2</sub> has been captured, the next challenge is to valorize this compound obtained in large proportions to give rise to other compounds that may be of great commercial interest. In this sense, several catalytic applications have been detailed in the literature such as the synthesis of fuels, drugs or building block molecules to obtain a wide range of valuable products. In addition, CO<sub>2</sub> can be also employed in photocatalytic process or artificial photosynthesis and in the polymers field [3,4].

In the carbon capture and storage (CCS) process, it has been reported that between 50–90% of the global cost is attributed to CO<sub>2</sub> capture [5] so one of the main efforts for the scientific community is associated to the development of efficient processes for CO<sub>2</sub> capture. Among technologies proposed for the CO<sub>2</sub> capture, it can be highlighted cryogenic distillation, membrane purification, absorption and adsorption [5]. Both cryogenic distillation and membrane purification appear highly efficient in short-scale; however, there are limitations for the larger-scale, as well as diluted CO<sub>2</sub>-flows. In addition, the cost of these processes is quite expensive for the large amounts of CO<sub>2</sub> that should be retained [6]. The most mature technology used to retain CO<sub>2</sub> molecules is absorption with amines or chilled ammonia obtaining excellent results, although a strong drawback is observed related to the high corrosivity and the costs required for the regeneration of the amines [7].



**Citation:** Cecilia, J.A.; Ballesteros Plata, D.; Vilarrasa García, E. CO<sub>2</sub> Valorization and Its Subsequent Valorization. *Molecules* **2021**, *26*, 500. <https://doi.org/10.3390/molecules26020500>

Received: 23 December 2020

Accepted: 14 January 2021

Published: 19 January 2021

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

The design of materials with the appropriate physicochemical properties seems to be the most sustainable technology for CO<sub>2</sub> capture. There is a wide range of adsorbents with the potential to capture CO<sub>2</sub>. However, it is necessary to highlight that the cost of CO<sub>2</sub> capture can reach 90% of the global cost of the CCS process so efficient materials for CO<sub>2</sub> capture are required, but at the same time these materials must be sustainable from an economic point of view. In this sense, alkaline and mainly alkaline-earth oxides have shown excellent behavior in CO<sub>2</sub> capture although these materials display a serious drawback related to their regeneration because of the strong interaction of these oxides with the CO<sub>2</sub> molecules [8]. On the other hand, a wide range of porous materials have been designed as molecular sieves and then tested in CO<sub>2</sub> adsorption processes. In the last decade, both metal organic frameworks (MOFs) and graphene organic frameworks (GOFs) have been developed to retain molecules [9,10]. These materials display 3D ordered structures with narrow and homogenous pore size in such a way that these porous materials can trap CO<sub>2</sub> molecules in their structures. The main drawbacks of these materials are related to the high cost of synthesizing adsorbents in large-scale and the relatively low thermal stability of MOFs and GOFs. Other materials with small and narrow pore diameter are zeolites and activated carbons. Both adsorbents have been synthesized on larger scale for several adsorption and catalysis processes, attaining high CO<sub>2</sub> adsorption capacity [11,12]. The design of porous silica with homogeneous and narrow pore distribution has also emerged in the last decades as adsorbent or catalytic support. In the same way, these porous silicas have been selected for CO<sub>2</sub> capture although the adsorption capacity was lower than that observed for the adsorbents indicated previously [13,14]. Clay minerals are other porous materials that have been tested to capture CO<sub>2</sub>. These materials have aroused great interest due to their low cost and high availability [15].

In all cases, these adsorbents can improve their adsorption capacity by the incorporation of amine-species. The main strategies reported in the literature are grafting with amine-alkoxisilanes [16] or the impregnation of amine-rich polymers [13,14]. In both cases, the CO<sub>2</sub> adsorption capacity increases because of the existence of chemical interactions via zwitterion forming carbamate in dry conditions or bicarbonate under wet conditions [5].

Nowadays, there are three approaches to CO<sub>2</sub> capture from the combustion of fossil fuels (precombustion, oxyfuel combustion, and postcombustion) [17,18]. Postcombustion CO<sub>2</sub> capture is well known from the 1970s as a potential economic source of CO<sub>2</sub> for enhanced oil recovery operations so this process is ready today while both precombustion and oxyfuel combustion are still in development [17,18].

The main efforts in the CCS process must be focused on the development of innovative technologies to increase the efficiency of the systems. In this sense, several parameters, such as the influence of the solvent, configuration of absorption and stripping columns, operating conditions of columns, percentage of CO<sub>2</sub> avoided, captured CO<sub>2</sub> purity and the regeneration steps, must be considered [3].

Once CO<sub>2</sub> is captured, the next challenge is its valorization into high-added value products. Generally, it has been reported that CO<sub>2</sub> can be valorized through physical utilization or chemical valorization to form valuable products [19].

As itself, CO<sub>2</sub> can be directly used to carbonate drinks, produce dry ice, refrigerant, welding medium or fire extinguishers, among others. However, these applications are limited so the effect on the mitigation of CO<sub>2</sub> emissions is negligible [3]. Pure or dissolved CO<sub>2</sub> can also be employed in enhanced oil recovery, enhanced gas recovery or enhanced geothermal systems.

When CO<sub>2</sub> is valorized from physical utilization, these molecules remain unaltered in their form pure or in solution without any chemical reaction.

Several authors pointed out that the injection of CO<sub>2</sub> or CH<sub>4</sub>/CO<sub>2</sub> improves oil recovery in homogeneous hydrocarbon reservoirs, so it is a promising alternative for the exploitation of oil reserves [20].

The integration of a methanol plant with enhanced gas recovery and geo-sequestration reported that CO<sub>2</sub> capture sequestration and utilization has the potential to digest a natural

fed gas with a maximum CO<sub>2</sub> mole fraction of 0.232 [21]. About 83.8% of the CO<sub>2</sub> captured was employed in enhanced gas recovery while 16.2% was employed in the production of fertilizers [22].

CO<sub>2</sub> has been also used as geo-fluid for enhanced geothermal systems to obtain geothermal energy [23]. On the other hand, CO<sub>2</sub> can be used as an alternative to synthetic refrigerants in air conditioning leading to highly efficient systems where fuel consumption diminished [24].

CO<sub>2</sub> can also be used as a feedstock in the synthesis of valuable chemicals and fuels. The use of CO<sub>2</sub> as a reactive can reduce resource consumption as well as lower the carbon footprint, leading to sustainable chemical processes.

CO<sub>2</sub> can react with CH<sub>4</sub> to form syngas through dry-reforming, which can satisfy the demands of valuable chemicals like naphtha or diesel among others [25]. Generally, the components of syngas are H<sub>2</sub> and CO, although small proportions of CO<sub>2</sub> and H<sub>2</sub>O can also be observed. The use of CO<sub>2</sub> in the reforming process allows the combination of steam-methane reforming and dry-methane reforming to reach the optimum H<sub>2</sub>/CO ratio [26]. CO<sub>2</sub> can also be used in the oxidation of CH<sub>4</sub>, obtaining high proportions of CO and H<sub>2</sub>, which can be used as feed in the reforming of syngas. The excess CO<sub>2</sub> obtained in the reaction tail can be recycled to the feed again. In the same way, CO<sub>2</sub> can be converted into CO from the reverse water gas shift reaction using In<sub>2</sub>O<sub>3</sub> and Ga<sub>2</sub>O<sub>3</sub> [27].

Methanol can be produced from CO<sub>2</sub> in the reforming stage (indirectly) and in the methanol reactor (directly) where syngas is converted to methanol [3,28]. CO<sub>2</sub> utilization in this process was about 0.12 t per metric ton of methanol. The installation of a reverse water gas shift reactor on the recycled stream improves methanol production as well as CO<sub>2</sub> consumption [29]. As itself, two molecules of methanol can be dehydrated to form dimethyl ether although it can also be formed from syngas directly [30]. The synthesis of methanol can also take place by a photoreduction of CO<sub>2</sub> and H<sub>2</sub>O [31].

Urea can also be formed from NH<sub>3</sub> and CO<sub>2</sub> via carbamide. It has been reported that the synthesis of one ton of urea could consume between 0.735–0.750 tonnes of CO<sub>2</sub>. These authors also indicated that the coproduction of urea and energy can take place simultaneously [3]. There are some studies where CO<sub>2</sub> coming from syngas of the underground coal gasifier was employed in the formation of carbamide [32], which is considered as an intermediate in the synthesis of the urea. However, the market price of this process is not competitive yet [33].

Dimethyl carbonate has been synthesized from the reaction of phosgene and methanol. However, the high toxicity of phosgene (COCl<sub>2</sub>) has led to the development of alternative synthetic strategies. Nowadays, there are several industrial processes where CO<sub>2</sub> is used as a reagent to form dimethyl carbonate. Between them, it can be highlighted direct production from methanol and CO<sub>2</sub>, production from CO<sub>2</sub> and ortho-ester or acetals and production from methanol, CO<sub>2</sub> and epoxides [34].

Polyurethane is formed by the reaction of CO<sub>2</sub> and propylene oxide with an alcohol as starter of the reaction and zinc hexacyanocobaltate as catalyst. The synthesis of polyurethane can be one of the most interesting applications to valorize CO<sub>2</sub> due to the high demand of this product in the market [35]. It has been reported that the amount of CO<sub>2</sub> employed in the synthesis of polyurethane was 0.3–1.7 kg CO<sub>2</sub>/kg polyurethane [36].

The conversion of syngas to obtain hydrocarbons from the Fischer–Tropsch process has been a challenge throughout the last century. Generally, CO is formed from CO<sub>2</sub> through the water gas shift reaction. Other authors have also proposed the cofeed of CO-CO<sub>2</sub> so a small amount of CO<sub>2</sub> is required to adjust the H<sub>2</sub>/CO ratio [37].

CO<sub>2</sub> can also be hydrogenated to form CH<sub>4</sub> via the Sabatier reaction. This reaction is very useful in the purification of syngas as well as in the purification of H<sub>2</sub> streams in polymer electrolyte fuel cell anodes [38].

Another promising innovative technology for CO<sub>2</sub> valorization is its use in the chemical-looping dry-reforming process, which consists of three stages (methane reduction, CO<sub>2</sub> reforming to form CO and oxidation) [39].

Mineralization of CO<sub>2</sub> to form carbonate species (CO<sub>3</sub><sup>2-</sup>) is a process where energy is released. This process can be used in cement manufacturing to produce green building materials [40].

Other reagents have been synthesized using CO<sub>2</sub> as reagent. Between them, ethylene oxide is a chemical formed from ethylene and CO<sub>2</sub>, which is highly used in the chemical industry, mainly in the synthesis of ethylenglycol [3]. In the same way, ethylene and CO<sub>2</sub> have also been employed to synthesize polyethylene. Supercritical CO<sub>2</sub> is also used for polybutylacrylate polymerization [3]. On the other hand, CO<sub>2</sub> can also be employed in the dehydrogenation of propane to propylene [41] or ethylbenzene to styrene [42]. In addition, CO<sub>2</sub> is also employed to synthesize furan-2,5-dicarboxylic acid, which is considered as a building block with applications in the field of polymers [43]. The CO<sub>2</sub> molecule can also react with epoxides favoring the ring-expansion or copolymerization reactions [44]. Another catalytic application of CO<sub>2</sub> is its use in oxidative catalytic activation of small alkanes [45].

In this editorial, the most representative applications have been highlighted. However, the number of applications is uncountable, mainly in fine chemistry or in the field of polymers as well as in the field of biology, since a wide variety of microorganisms can assimilate CO<sub>2</sub> in anaerobic reactions such as methanation.

The abatement of CO<sub>2</sub> emissions is an exciting challenge for the scientific community. The objective of solving the problem of global warming can be accompanied by the use and recovery of CO<sub>2</sub> in value-added compounds. Most of the processes devised to recover CO<sub>2</sub> are relatively recent in such a way that they are processes that must be optimized to be sustainable and competitive. The greatest efforts should be focused on the integration of processes to save transportation costs. For this purpose, these processes must be supported by environmental policies that promote the capture and valorization of CO<sub>2</sub>.

**Funding:** 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.

**Acknowledgments:** J.A.C. and D.B.P. thank the financial support to the project RTI2018-099668-BC22 of Ministerio de Ciencia, Innovación y Universidades and FEDER funds. E.V.G. thanks the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, National Council for Scientific and Technological Development, Brazil) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES, Higher Education Personnel Improvement Coordination, Brazil) for financial support.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Masson Delmotte, V.; Zhai, P.; Pörtner, H.O.; Roberts, D.; Skea, J.; Shukla, P.R.; Pirani, A.; Moufouma-Okia, W.; Pean, C.; Pidcock, R.; et al. *An IPCC Special Report on the Impacts of Global Warming of 1.5 °C above Pre-Industrial Levels and Related Global Greenhouse Gas Emission Pathways, in the Context of Strengthening the Global Response to the Threat of Climate Change, Sustainable Development, and Efforts to Eradicate Poverty*; Masson Delmotte, V., Zhai, P., Pörtner, H.O., Roberts, D., Skea, J., Shukla, P.R., Pirani, A., Moufouma-Okia, W., Pean, C., Pidcock, R., et al., Eds.; IPCC: Geneva, Switzerland, 2018.
2. Song, C.; Liu, Q.; Ji, N.; Deng, S.; Zhao, J.; Li, Y.; Song, Y.; Li, H. Alternative pathways for efficient CO<sub>2</sub> capture by hybrid processes—A review. *Renew. Sustain. Energy Rev.* **2018**, *82*, 215–231. [[CrossRef](#)]
3. Rafiee, A.; Khalilpour, K.R.; Milani, D.; Panahi, M. Trends in CO<sub>2</sub> conversion and utilization: A review from process systems perspective. *J. Environ. Chem. Eng.* **2018**, *6*, 5771–5794. [[CrossRef](#)]
4. Ravanchi, M.T.; Sahebdehfar, S. Catalytic conversions of CO<sub>2</sub> to help mitigate climate change: Recent process developments. *Process. Saf. Environ.* **2010**, *145*, 172–194. [[CrossRef](#)]
5. Pera-Titus, M. Porous Inorganic Membranes for CO<sub>2</sub> Capture: Present and Prospects. *Chem. Rev.* **2013**, *114*, 1413–1492. [[CrossRef](#)] [[PubMed](#)]
6. Choi, S.; Drese, J.D.; Jones, C.W. An efficient and effective convolutional auto-encoder extreme learning machine network for 3d feature learning. *Neurocomputing* **2018**, *174*, 49–61.
7. Darde, V.; Thomsen, K.; Van Well, W.J.M.; Stenby, E.H. Chilled ammonia process for CO<sub>2</sub> capture. *Energy Procedia* **2009**, *1*, 1035–1042. [[CrossRef](#)]
8. Wang, S.; Yan, S.; Ma, X.; Gong, J. Recent advances in capture of carbon dioxide using alkali-metal-based oxides. *Energy Environ. Sci.* **2011**, *4*, 3805–3819. [[CrossRef](#)]

9. Sumida, K.; Rogow, D.L.; Mason, J.A.; McDonald, T.M.; Bloch, E.D.; Herm, Z.R.; Bae, T.-H.; Long, J.R. Carbon Dioxide Capture in Metal–Organic Frameworks. *Chem. Rev.* **2012**, *112*, 724–781. [[CrossRef](#)]
10. Haque, E.; Islam, M.; Pourazadi, E.; Sarkar, S.; Harris, A.T.; Minett, A.I.; Yanmaz, E.; AlShehri, S.M.; Ide, Y.; Wu, K.C.-W.; et al. Boron-Functionalized Graphene Oxide–Organic Frameworks for Highly Efficient CO<sub>2</sub> Capture. *Chem. Asian J.* **2017**, *12*, 283–288. [[CrossRef](#)]
11. Merel, J.; Clause, M.; Meurier, F. Experimental investigation on CO<sub>2</sub> post-combustion capture by indirect thermal swing adsorption using 13X and 5A zeolites. *Ind. Eng. Chem. Res.* **2008**, *47*, 209–215. [[CrossRef](#)]
12. Pevida, C.; Plaza, M.G.; Arias, B.; Feroso, J.; Rubiera, F.; Pis, J.J. Surface modification of activated carbons for CO<sub>2</sub> capture. *Appl. Surf. Sci.* **2008**, *254*, 7165–7172. [[CrossRef](#)]
13. Vilarrasa-García, E.; Cecilia, J.A.; Moura, P.A.S.; Azevedo, D.C.S.; Rodríguez-Castellón, E. Assessing CO<sub>2</sub> Adsorption on Amino-Functionalized Mesocellular Foams Synthesized at Different Aging Temperatures. *Front. Chem.* **2020**, *8*, 591766. [[CrossRef](#)] [[PubMed](#)]
14. Cecilia, J.A.; Vilarrasa-García, E.; Morales-Ospino, R.; Bastos-Neto, M.; Azevedo, D.C.S.; Rodríguez-Castellón, E. Insights into CO<sub>2</sub> adsorption in amino-functionalized SBA-15 synthesized at different aging temperature. *Adsorption* **2020**, *26*, 225–240. [[CrossRef](#)]
15. Chouikhi, N.; Cecilia, J.A.; Vilarrasa-García, E.; Besghaier, S.; Chlendi, M.; Franco-Duro, F.I.; Rodríguez-Castellón, E.; Bagane, M. CO<sub>2</sub> adsorption of materials synthesized from clay minerals: A review. *Minerals* **2019**, *5*, 514. [[CrossRef](#)]
16. Hiyoshi, N.; Yogo, Y.; Yashima, T. Adsorption characteristics of carbon dioxide on organically functionalized SBA-15. *Microporous Mesoporous Mater.* **2005**, *84*, 357–365. [[CrossRef](#)]
17. Desideri, U.; Paolucci, A. Performance modelling of a carbon dioxide removal system for power plants. *Energy Convers. Manag.* **1999**, *40*, 1899–1915. [[CrossRef](#)]
18. Rao, A.B.; Rubin, E.S. A Technical, Economic, and Environmental Assessment of Amine-Based CO<sub>2</sub> Capture Technology for Power Plant Greenhouse Gas Control. *Environ. Sci. Technol.* **2002**, *36*, 4467–4475. [[CrossRef](#)]
19. Huang, C.H.; Tan, C.S. A Review: CO<sub>2</sub> Utilization. *Aerosol Air Qual. Res.* **2014**, *14*, 480–499. [[CrossRef](#)]
20. Safi, R.; Agarwal, R.K.; Banerjee, S. Numerical simulation and optimization of CO<sub>2</sub> utilization for enhanced oil recovery from depleted reservoirs. *Chem. Eng. Sci.* **2016**, *144*, 30–38. [[CrossRef](#)]
21. Luu, M.T.; Milani, D.; Abbas, A. Analysis of CO<sub>2</sub> utilization for methanol synthesis integrated with enhanced gas recovery. *J. Clean. Prod.* **2016**, *112*, 3540–3554. [[CrossRef](#)]
22. Nakaten, N.; Islam, R.; Kempka, T. 12th international conference on greenhouse gas control technologies, GHGT-12 Underground coal gasification with extended CO<sub>2</sub> utilization—An economic and carbon neutral approach to tackle energy and fertilizer supply shortages in Bangladesh. *Energy Procedia* **2014**, *63*, 8036–8043. [[CrossRef](#)]
23. Zhang, F.Z.; Xu, R.N.; Jiang, P.X. Thermodynamic analysis of enhanced geothermal systems using impure CO<sub>2</sub> as the geofluid. *Appl. Therm. Eng.* **2016**, *99*, 1277–1285. [[CrossRef](#)]
24. Antonijević, D.L. Carbon dioxide as the replacement for synthetic refrigerants in mobile air conditioning. *Therm. Sci.* **2008**, *12*, 55–64. [[CrossRef](#)]
25. Rafiee, A.; Panahi, M.; Khalilpour, K.R. CO<sub>2</sub> utilization through integration of post-combustion carbon capture process with Fischer-Tropsch gas-to-liquid (GTL) processes. *J. CO<sub>2</sub> Util.* **2017**, *18*, 98–106. [[CrossRef](#)]
26. Lim, Y.; Lee, C.J.; Jeong, Y.S.; Song, I.H.; Lee, C.J.; Han, C. Optimal Design and Decision for Combined Steam Reforming Process with Dry Methane Reforming to Reuse CO<sub>2</sub> as a Raw Material. *Ind. Eng. Chem. Res.* **2012**, *51*, 4982–4989. [[CrossRef](#)]
27. Chen, W.H.; Lin, S.C. Characterization of catalytic partial oxidation of methane with carbon dioxide utilization and excess enthalpy recovery. *Appl. Energy* **2016**, *162*, 1141–1152. [[CrossRef](#)]
28. Sun, Q.; Ye, J.; Liu, C.J.; Ge, Q. In<sub>2</sub>O<sub>3</sub> as a promising catalyst for CO<sub>2</sub> utilization: A case study with reverse water gas shift over In<sub>2</sub>O<sub>3</sub>. *Greenh. Gases Sci. Technol.* **2014**, *4*, 140–144. [[CrossRef](#)]
29. Kim, W.S.; Yang, D.R.; Moon, D.R.; Ahn, B.S. The process design and simulation for the methanol production on the FPSO (floating production, storage and off-loading) system. *Chem. Eng. Res. Des.* **2018**, *92*, 931–940. [[CrossRef](#)]
30. Catizzone, E.; Bonura, E.; Migliori, M.; Frusteri, F.; Giordano, G. CO<sub>2</sub> recycling to dimethyl ether: State-of-the-art and perspectives. *Molecules* **2018**, *23*, 31. [[CrossRef](#)]
31. Nazimek, D.; Czech, B. Artificial photosynthesis—CO<sub>2</sub> towards methanol. *IOP Conf. Ser. Mater. Sci. Eng.* **2011**, *19*, 012010. [[CrossRef](#)]
32. Kempka, T.; Plötz, M.L.; Schlüter, R.; Hamann, J.; Deowan, S.A.; Azzam, R. Carbon dioxide utilisation for carbamide production by application of the coupled UCG-urea process. *Energy Procedia* **2011**, *4*, 2200–2205. [[CrossRef](#)]
33. Huang, S.; Yan, B.; Wang, S.; Ma, X. Recent Advances in Dialkyl Carbonates Synthesis and Applications. *Chem. Soc. Rev.* **2015**, *44*, 3079–3116. [[CrossRef](#)] [[PubMed](#)]
34. Laurency, G.; Picquet, M.; Plasseraud, L. Di-n-butyltin(IV)-catalyzed dimethyl carbonate synthesis from carbon dioxide and methanol: An in situ high pressure <sup>119</sup>Sn{1H} NMR spectroscopic study. *J. Organomet. Chem.* **2011**, *696*, 1904–1909. [[CrossRef](#)]
35. Langanke, J.; Wolf, A.; Hofmann, J.; Böhm, K.; Subhani, M.A.; Müller, T.E.; Leitner, W.; Gurtler, C. Carbon dioxide (CO<sub>2</sub>) as sustainable feedstock for polyurethane production. *Green Chem.* **2014**, *16*, 1865–1870. [[CrossRef](#)]
36. Assen, N.V.D.; Sternberg, A.; Käthelhön, A.; Bardow, A. Environmental potential of carbon dioxide utilization in the polyurethane supply chain. *Faraday Discuss.* **2015**, *183*, 291–307. [[CrossRef](#)]
37. Van Der Giesen, C.; Kleijn, R.; Kramer, G.J. Energy and Climate Impacts of Producing Synthetic Hydrocarbon Fuels from CO<sub>2</sub>. *Environ. Sci. Technol.* **2014**, *48*, 7111–7121. [[CrossRef](#)]

38. Sahebdehfar, S.; Takht Ravanchi, M. Carbon dioxide utilization for methane production: A thermodynamic analysis. *J. Pet. Sci. Eng.* **2015**, *134*, 14–22. [[CrossRef](#)]
39. Huang, Z.; Jiang, H.; He, F.; Chen, D.; Wei, G.; Zhao, K.; Zheng, A.; Feng, Y.; Zhao, Z.; Li, H. Evaluation of multi-cycle performance of chemical looping dry reforming using CO<sub>2</sub> as an oxidant with Fe–Ni bimetallic oxides. *J. Energy Chem.* **2016**, *25*, 62–70. [[CrossRef](#)]
40. Ebrahimi, A.; Saffari, M.; Milani, D.; Montoya, A.; Valix, M.; Abbas, A. Sustainable transformation of fly ash industrial waste into a construction cement blend via CO<sub>2</sub> carbonation. *J. Clean. Prod.* **2017**, *156*, 660–669. [[CrossRef](#)]
41. Michorczyk, P.; Ogonowski, J. Dehydrogenation of propane in the presence of carbon dioxide over oxide-based catalysts. *React. Kinet. Catal. Lett.* **2003**, *78*, 41–47. [[CrossRef](#)]
42. Noh, J.; Chang, J.S.; Park, J.N.; Lee, K.Y.; Park, S.E. CO<sub>2</sub> utilization for the formation of styrene from ethylbenzene over zirconia-supported iron oxide catalysts. *Appl. Organomet. Chem.* **2000**, *14*, 815–818. [[CrossRef](#)]
43. Terzopoulos, Z.; Papadopoulos, L.; Zamboulis, A.; Papageorgiou, D.G.; Papageorgiou, G.Z.; Bikiaris, D.N. Tuning the Properties of Furandicarboxylic Acid-Based Polyesters with Copolymerization: A Review. *Polymers* **2020**, *12*, 1209. [[CrossRef](#)] [[PubMed](#)]
44. Buckley, B.R.; Patel, A.P.; Wijayantha, K.G.U. Ring-expansion addition of epoxides using applied potential: An investigation of catalysts for atmospheric pressure carbon dioxide utilization. *RSC Adv.* **2014**, *4*, 58581–58590. [[CrossRef](#)]
45. Wang, S.; Zhu, Z.H. Catalytic conversion of alkanes to olefins by carbon dioxide oxidative dehydrogenation. A review. *Energy Fuels* **2004**, *18*, 1126–1139. [[CrossRef](#)]