

Review

The Role of CO₂ as a Mild Oxidant in Oxidation and Dehydrogenation over Catalysts: A Review

Sheikh Tareq Rahman ¹, Jang-Rak Choi ^{1,2}, Jong-Hoon Lee ¹ and Soo-Jin Park ^{1,*}

¹ Department of Chemistry, Inha University, 100 Inharo, Incheon 22212, Korea; rahman19@inha.edu (S.T.R.); 22161120@inha.edu (J.-R.C.); boy834@naver.com (J.-H.L.)

² Evertch Enterprise Co. Ltd., Dongtansandan 2 gil, Hwaseong 18487, Korea

* Correspondence: sjpark@inha.ac.kr; Tel.: +82-32-876-7234

Received: 28 July 2020; Accepted: 8 September 2020; Published: 17 September 2020



Abstract: Carbon dioxide (CO₂) is widely used as an enhancer for industrial applications, enabling the economical and energy-efficient synthesis of a wide variety of chemicals and reducing the CO₂ levels in the environment. CO₂ has been used as an enhancer in a catalytic system which has revived the exploitation of energy-extensive reactions and carry chemical products. CO₂ oxidative dehydrogenation is a greener alternative to the classical dehydrogenation method. The availability, cost, safety, and soft oxidizing properties of CO₂, with the assistance of appropriate catalysts at an industrial scale, can lead to breakthroughs in the pharmaceutical, polymer, and fuel industries. Thus, in this review, we focus on several applications of CO₂ in oxidation and oxidative dehydrogenation systems. These processes and catalytic technologies can reduce the cost of utilizing CO₂ in chemical and fuel production, which may lead to commercial applications in the imminent future.

Keywords: carbon dioxide; soft oxidant; oxidation; dehydrogenation; nano-catalyst

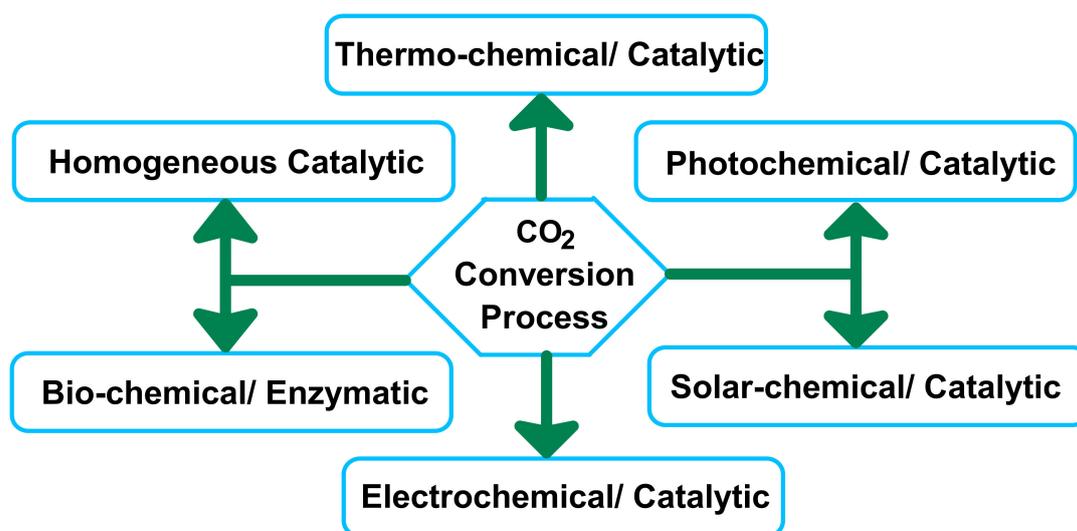
1. Introduction

Global warming is an imminent threat to our planet. It is essential to diminish the emission of greenhouse gases, especially carbon dioxide (CO₂), to slow global warming. Different sources of CO₂ emissions are a significant part to dictate by the ignition of liquid, solid, and gaseous chemicals. Rising atmospheric CO₂ concentrations and the increasing temperature of the planet's surface have increased public awareness of this problem [1]. CO₂ is utilized in the in the manufacturing industries, which is mostly released by the combustion of fossil fuels [2]. Among different products, methanol and formic acid can be synthesized from CO₂ which is used directly as fuels or to generate H₂ on demand at low temperatures (<100 °C) [1]. However, CO₂ can be used efficiently in various value-adding strategies and research pursuits which are converted waste emissions into valuable chemicals products, such as hydrocarbons and oxygenates [3]. Electrochemical activation technologies and conversion of CO₂ and H₂O into hydrocarbons has seen a marked increase in research activity over the past few years [4]. The impressive separation and utilization of CO₂ technologies in a higher challenge of organizing than other gases [5]. The development of CO₂ for novel approaches can add value to CO₂ recycling as it may result in commercially useful carbon-based products. Today, CO₂ is used commercially in the production of pharmaceuticals, air-conditioning systems, beverages, fertilizers, inert agents for food packaging, the water treatment process, fire extinguishers, and other applications. To achieve sustainable economic growth, it is crucial to study the conversion of CO₂ into carbon-based chemicals and materials. Industrial companies use massive amounts of CO₂ to enhance oil restoration. Biomass conversion to fuels also utilizes CO₂ [6]. Recently, Drisdell et al. [7] reported that oxide-derived copper catalysts are better at making fuel products from CO₂. According to Drisdell group, CO₂ is initially converted into carbon monoxide under first conditions for producing fuel and then hydrocarbon chains

are developed. Oxide-derived catalysts are better, not because they have oxygen remaining while they reduce carbon monoxide, but because the process of removing the oxygen creates a metallic copper structure that is better at forming ethylene. Using solar energy to convert CO₂ into most needed fuels has the potential to decrease global warming impact (GWI) and produce sustainable fuels at large scale [8]. A great deal of research has focused on combining heteroatoms in the carbon structure to improve the exchangeable action of CO₂ along with the adsorbent surfaces over the past few years [6].

CO₂ utilization has recently become an alluring sector of research, as it will help to alleviate climate change and reduce industrial operating costs. Globally, CO₂ capture and utilization are significant goals for chemicals and materials scientists [9]. Researchers are working to diminish the negative effects of CO₂ by adsorption [10,11], reduction, and fixation as well as through the development of metal-organic frameworks (MOFs), zeolites, polymers and micro-porous carbons [12]. Currently, CO₂ is used in an impenetrable phase under harsh conditions as an active promoter, making it a green substitute for organic compounds [13]. There are several limitations of dense phase CO₂ media, including the high pressures required to assure sufficient solubility of various transition metal catalysts and low reaction rates [14]. Jessop et al. proposed, as a solution to the solubility issue, an exchangeable process using 1,8-diazabicyclo-[5.4.0]-undec-7-ene. Additionally, they were able to eliminate partition steps by adjusting polarities with the use of CO₂ [15]. Another way to utilize CO₂ is to use it as an oxygen source. Park et al. demonstrated the mild oxidant character of CO₂ in the oxidative dehydrogenation of various types of alkyl benzene in both liquid and gaseous phases [16,17]. Using CO₂ in catalytic reactions offers other advantages; for instance, absorption of hydrogen from alkanes, alkyl aromatics, and alcohols using CO₂ as a reactant to create CO and oxygen species results in an expedited reaction rate, increased conversion, higher yield, and suppression of oxidation [16]. The presence of both CO₂ and O₂ increases the reaction rates as well as the conversion and selectivity. This process is performed under subcritical pressures of CO₂ and involves CO₂-promoted systems (CPS) instead of a CO₂-expanded system, as evidenced by the low-pressure approach as well as catalytic CO₂ activation. Recently developed CO₂ use technologies require the utilization of high-energy initiators [18]. Although great progress has been made in the carbon dioxide sector, there remain innate limitations, such as high-energy requirements, and the hydrogen recession. CO₂ has various benefits as a mild oxidant over several oxidizing promoters tested for oxidative dehydrogenation reaction, such as dry air, SO₂, and N₂O [19]. C1 products such as methanol, formic acid has become possible to produce with high initial selectivity by using CO₂ over simple metal-based catalysts [4]. CO₂ promotes selectivity by contaminating the non-selective species of several catalysts, preventing the production of several by-products [20]. Additionally, CO₂ is used as a carbon source in the decoking process ($C + CO_2 = 2CO$) which sustains catalytic activity [21]. Therefore, the oxidative dehydrogenation (ODH) reaction with CO₂ primarily considered to be a gas-interposed adaptation of the catalyst surface. This affects the diffusion, adsorption, and red-ox characteristics of the catalyst [22]. In recent years, the CO₂ conversion process has been utilized in various sectors, including thermo-chemical [23], photochemical [24], solar-chemical [25], electrochemical [26], biochemical [27] and homogenous catalysis [28] (Scheme 1).

In this review, we discuss a way to improve various technologies using CO₂ as a mild oxidant and enhancer for the production of essential chemicals. The purpose of this review is to illustrate the limitations and scope of CO₂ utilization and to highlight the advantages and challenges of carbon management. The use of CO₂ as a feedstock is a major goal, which could have a modest impact in practice, but may impart a significant symbolic effect on worldwide carbon stability. The further impact would result from the use of CO₂ as a soft oxidant and for oxidative dehydrogenation in catalytic reactions. Bartholomew et al. [29] studied the oxidizing capability of different gases in the gasification of coke. Their activities were ranked as follows: O₂ (105) > H₂O (3) > CO₂ (1) > H₂ (0.003). This demonstrates that carbon dioxide is less active than molecular oxygen and water, but still offers high oxidative capacity. However, carbon dioxide has the greatest heat capability among the commonly used alternative gases. Furthermore, CO₂ can reduce the occurrence of hotspots, which cause problems, such as catalyst deactivation, runaway temperature, and undesirable product oxidation.



Scheme 1. The various chemical processes for CO₂ conversion.

2. Effect of CO₂ in Oxidation

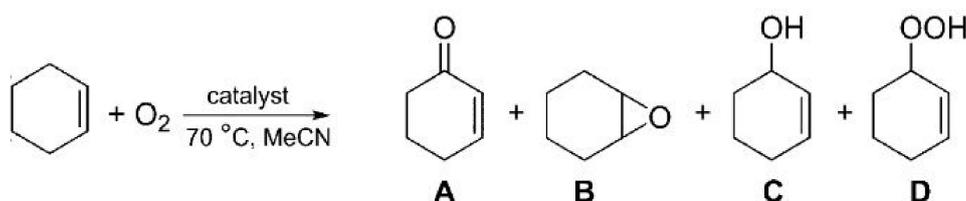
2.1. Influence of CO₂ on Oxidation of Cyclohexene

The impact of CO₂, at various concentrations, was investigated on the oxidation of cyclohexene which is a small and symmetric molecule, similar to many starting compounds in chemical synthesis (Scheme 2) [30]. The results revealed that O₂/CO₂ conversion (%) was higher than O₂/N₂ conversion (%) rate. However, at a gas ratio of 0.066 O₂:CO₂/N₂ (Table 1, entry 1), cyclohexene was not converted. Park et al. revealed the positive impact of carbon dioxide on mesoporous metal-free oxidation carbon nitride (MCN) catalysts [31]. These mesoporous MCN elements exhibit oxygen-carrying capabilities which are effective sites for oxidation. Additionally, the large nitrogen quantity in the CN matrix acts as a CO₂-philic exterior for the incitation of CO₂. Molecular oxygen promotes this synergy, allowing for the oxidation of cyclic olefins and improving the conversion of cyclic olefins with better selectivity. In-between the conversion of the O₂/CO₂ and the O₂/N₂, Park et al. observed the enhance performance as a premier time, which can be expressed as ΔC (%) and can be calculated using the Equation (1):

$$\Delta C(\%) = \frac{(C_{O_2/CO_2}) - (C_{O_2/N_2})}{(C_{O_2/CO_2}) + (C_{O_2/N_2})} \times 100 \quad (1)$$

where,

$$(C_{O_2/CO_2}) = \text{Conversion in } O_2/CO_2 \text{ and } (C_{O_2/N_2}) = \text{Conversion in } O_2/N_2$$



Scheme 2. Cyclohexene oxidation reaction over catalyst. (Redrawn from [30]; copyright (2018), WILEY-VCH). (A) = 2-cyclohexene-1-one, (B) = cyclohexene oxide, (C) = 2-cyclohexene-1-ol, (D) = 2-cyclohexene-1-hydroperoxide). Reaction conditions: 10 bar O₂; 2.5 mL cyclohexene; 0.5 mL cyclohexane(IS); 10 mg catalyst; 15 mL MeCN; stirred in an autoclave (1000 rpm); 70 °C; 16 h.

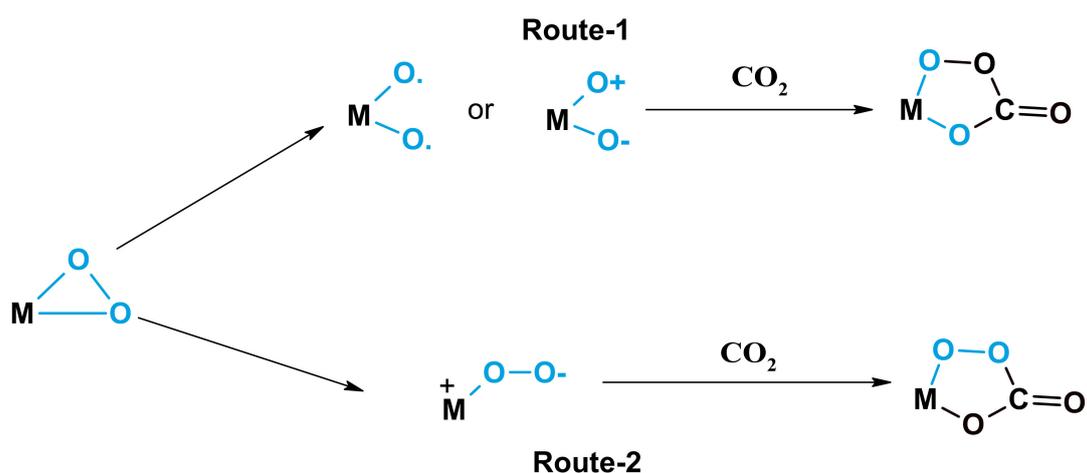
Table 1. Effect of the CO₂ on oxidation of cyclohexene over MCN Ref [31] (Reproduced from [31]; copyright (2011), Royal Society of Chemistry).

| Entry | Gas Ratio (PSI) ^a | Conversion (%) O ₂ /CO ₂ | Conversion (%) O ₂ /N ₂ | ΔC(%) ^b |
|-------|------------------------------|--|---|--------------------|
| 1 | 0.066 | 0 | 0 | 0 |
| 2 | 0.142 | 16 | 9 | 28 |
| 3 | 0.230 | 25 | 18 | 16.3 |
| 4 | 0.333 | 33 | 24 | 15.7 |
| 5 | 0.454 | 34 | 24 | 15.7 |

Reaction conditions: 20 mg Melamine mesoporous carbon nitride (M-MCN), 10 mL Dimethylformamide (DMF), temperature 373 K, Pressure 80 PSI, time 10 h; Estimated by Gas Chromatography (GC) analysis. ^a PSI = Pounds per Square Inch, ^b Conversion (%) of cyclic olefin.

The efficiency of CO₂ in the oxidation of cyclohexene at varying CO₂ concentrations is shown in Table 1. Higher conversions were achieved by the O₂/CO₂ system. The results showed that the conversion of cyclohexene was nothing at a content of 0.066 O₂ (entry 1). This is Possibly due to the low frictional pressure of O₂, which is deficient to drive the reaction. Further, the ΔC% value was higher for higher concentrations of CO₂. No meaningful change of ΔC% was demonstrated for gas ratios beyond 0.333 in the catalytic process, demonstrating the impregnation of activity.

CO₂ has been used with metal-supported systems that were observed to produce a per-oxycarbonate species which are highly active in oxidation reactions. Aresta et al. were reported the composition of a metal per-oxycarbonate species, as determined by spectroscopic analysis [32]. A process for the production of per ox-carbonate has acceded in Scheme 3. Park et al. investigated the oxidation of alkyl aromatics via an EPR analysis using a metal carbonate catalyst. They demonstrated the production of metal per-oxycarbonate groups in the presence of carbon dioxide by the hyperfine cracking of manganese. Yoo et al. [20] observed the production of per-oxycarbonate on Fe/Mo/DBH (deboronated borosilicate molecular sieve); the production of per-oxycarbonate is illustrated in Figure 1. All of the catalytic schemes discussed above involve transitional metal catalysts and CO₂ coupled with oxygen. The resulting enhancement over traditional metal oxide systems in O₂/CO₂ mixtures may occur because of an oxygen exchange between O₂ and CO₂, which would increase the rate of the reaction. During isotope-labeling studies, these types of exchanges have been detected by Iwata et al. [33] using different metal oxide structures.

**Scheme 3.** Per-oxycarbonate production reaction mechanisms (Redrawn from [32]; copyright (1996), American Chemical Society).

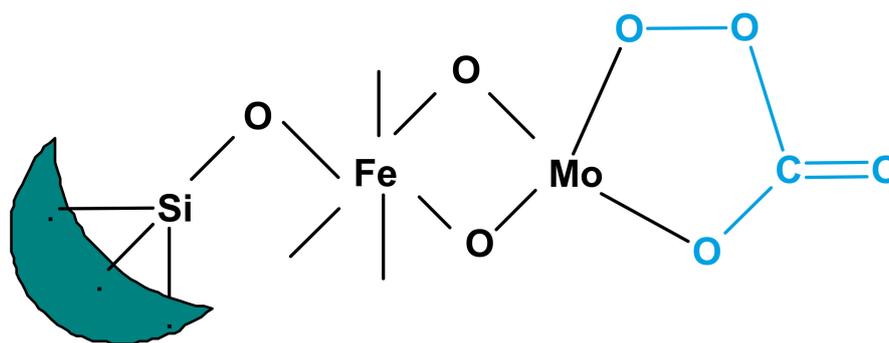
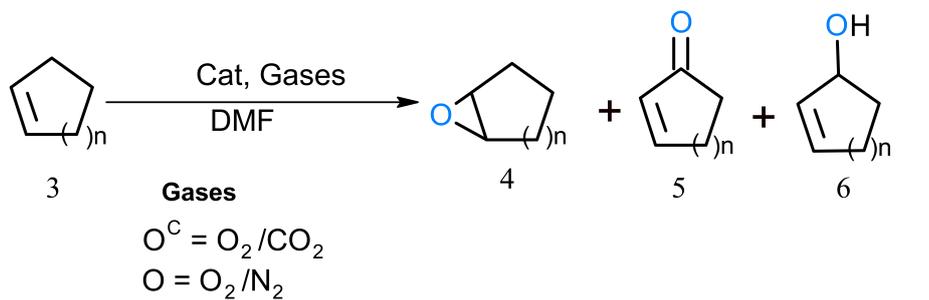


Figure 1. Per ox-carbonate over Fe/Mo/DBH in the O_2/CO_2 system (Reproduced from [20]; copyright (1993), Elsevier (Amsterdam, The Netherlands)).

2.2. Promotional Effect of CO_2 on Oxidation of Cyclic Olefins

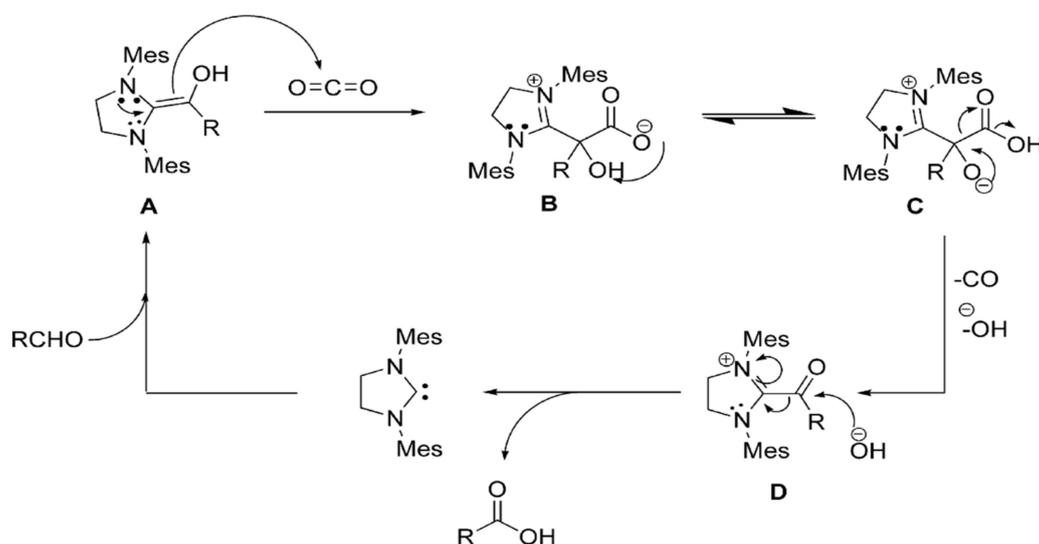
Park et al. demonstrated the use of CO_2 as a promoter for the oxidation of cyclic olefins with mesoporous carbon nitrides (CN) as a metal-free catalyst in the presence of molecular oxygen. Analysis of the surface characteristics of the catalyst after the reaction revealed the presence of carbamate, confirmed by a new band in the FTIR spectrum at 1419 cm^{-1} . This measurement illustrated the incitation of CO_2 owing to the accumulation of surface carbamate. This surface carbamate can then react with the cyclic olefins, assisted by the catalyst. After the reaction, the IR spectra showed the presence of extra bands at 2174 and 2115 cm^{-1} , possibly due to a gaseous CO doublet. However, these absorption bands were not present before the reaction. This analysis exposed the production of CO, which is revealed to the increased catalytic activity to credit to carbon dioxide sharing as an ‘oxygen atom’ onset [31,32]. The production of CO was previously observed in nitrogen including heterocyclic systems [34–36]. The positive impact of CO_2 in the oxidation of cyclic olefin was quantified by measuring the catalytic performance using various reactants, cyclopentene ($n = 1$), cyclohexene ($n = 2$), cyclooctene ($n = 4$), and cyclododecene ($n = 8$) (Table 2). The epoxide selectivity was greater in O_2/CO_2 than O_2/N_2 , suggesting that in the presence of CO_2 , the mechanism may be altered to improve the conversion and selectivity. The blend of gaseous from the autoclave was studied by IR spectroscopy to better understand the positive impact of CO_2 . In the reaction with no oxidant and source oxygen, it was presumed that CO_2 is reduced to CO and aldehyde is oxidized to carboxylic acid in the same process. The reaction may have occurred via the addition of carbon dioxide to the quickly produced Breslow intermediate A to produce the hydroxy carboxylate B and the tautomer C (Scheme 4) [34]. Possibly, the following intermediate can lose CO and hydroxide to support benzoic acid. Additionally, it was observed that intermediate D is supplicated in the oxidative esterification of aldehydes with CO. Interestingly, phenylglyoxylic acid was revealed to nucleophilic heterocyclic carbenes (NHC) under similar experimental conditions wherein phenylglyoxylic acid was switched to benzoic acid. (Scheme 5). Under mild experimental conditions, CO_2 was utilized in an NHC-intermediated conversion of the aldehyde to the carboxylic acid.

Table 2. Enhance role of CO₂ on cyclic olefins oxidation (Reproduced from [31]; copyright (2011), Royal Society of Chemistry).

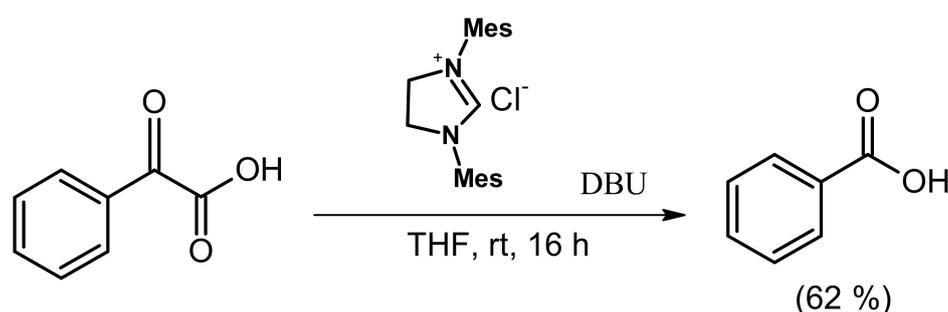


| Entry | n | Gas | Conversion of 3 (%) | Selectivity (%) | | | |
|-------|---|----------------|---------------------|-----------------|----|----|--------|
| | | | | 4 | 5 | 6 | ΔC (%) |
| 1 | 1 | O ^C | 40 | 37 | 24 | 29 | 12.6 |
| | | O | 31 | 30 | 22 | 40 | - |
| 2 | 2 | O ^C | 33 | 30 | 21 | 49 | 15.8 |
| | | O | 24 | 25 | 16 | 53 | - |
| 3 | 4 | O ^C | 21 | > 99 | - | - | 27.0 |
| | | O | 12 | > 99 | - | - | - |
| 4 | 8 | O ^C | 17 | > 99 | - | - | 30.7 |
| | | O | 9 | > 99 | - | - | - |

Reaction conditions: 20 mg Melamine mesoporous carbon nitride (M-MCN), 10 mL Dimethylformamide (DMF), temperature 373 K, Pressure 80 PSI, gas ratio 0.333, time 10 h; Produced analyzed by GC and GC-MS.



Scheme 4. Proposed Mechanism for aldehyde assisted CO₂ to carboxylic acid process. (Reprinted from [34]; copyright (2010), American Chemical Society).

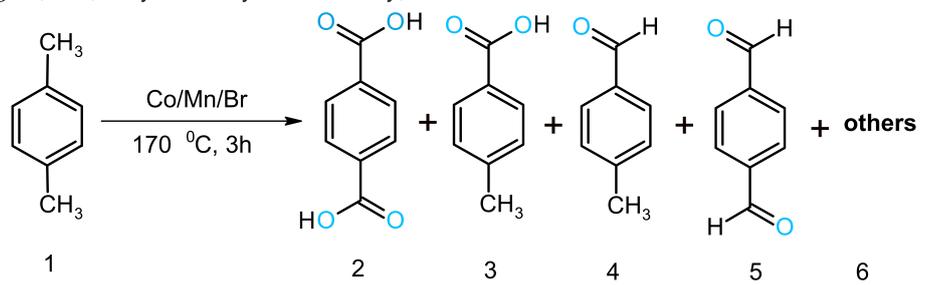


Scheme 5. Phenylglyoxylic acid to benzoic acid reaction with NHC-intermediate. (Reprinted from [34]; copyright (2010), American Chemical Society).

2.3. Influence of CO₂ on Oxidation of *p*-Xylene

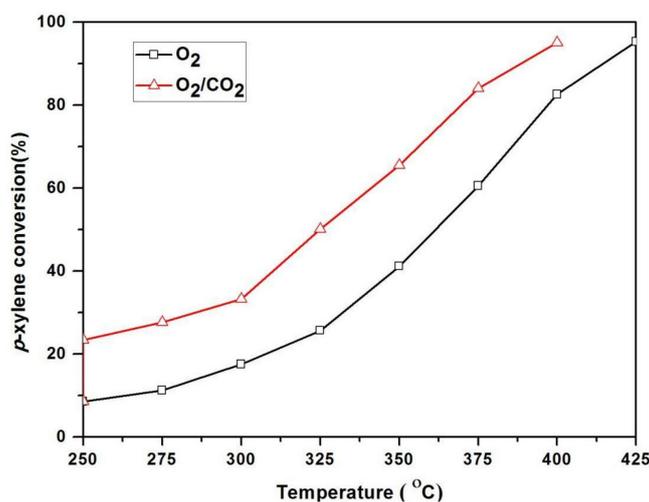
It was proposed that in the O₂-CO₂ system, metal peroxy-carbonate groups assist as oxygen transfer promoters to the oxyphilic substrate. Aresta et al. [32] also reported that the presence of O-O bonds in Rh (η^2 -O₂) complexes imply the accumulation of metal per-oxycarbonate during the other oxidation reaction. They demonstrated that CO₂ promotes the oxidative ability of O₂ over the RhCl(Pet₂-Ph)₃ catalyst. In the presence of CO₂ over the metal-based structure was found to be formation of peroxycarbonate species which are more active than hydrogen peroxide in oxidation reaction [37]. Park et al. [22] reported the performance of carbon dioxide in the liquid-phase oxidation reaction of toluene, *p*-tolu-aldehyde, and *p*-xylene with O₂ over an MC-based catalyst (Co/Mn/Br). The reaction rate, selectivity, and the conversion were all enhanced by the co-presence of CO₂. This enhancement was attributed to the creation of per-oxycarbonate species, as determined by electron paramagnetic resonance (EPR) analysis of the reaction with and without carbon dioxide. A hyperfine manganese arrangement was noticed in the existence of CO₂, confirming the formation of a per-oxycarbonate species.

Additionally, Park et al. observed the oxidation of different alkyl aromatics applying MC-supported catalysts [22]. Oxidations were carried out using O₂ as the oxidant (with N₂) and compared to reactions in the presence of both O₂ and CO₂. The conversion of *p*-xylene without CO₂ (Table 3) was 57.2%, whereas the conversion of *p*-xylene was increased to 66.8% in the presence of CO₂. Moreover, in O₂/CO₂, the yield of terephthalic acid was improved. The Amoco Chemical Research Laboratory studied the activation of CO₂ in the gas-state of *p*-xylene oxidation to *p*-tolualdehyde and terephthaldehyde over the chemical vapor deposition (CVD) of Fe/Mo/DBH [20]. The oxidation reaction was performed in two feed streams varying compositions, including *p*-xylene with O₂/N₂/He and *p*-xylene with O₂/N₂/CO₂. The catalytic activity is shown in both the feeds at various temperatures in Figure 2, as shown in the figure, *p*-xylene conversion in the existence of CO₂ in O₂ was greater than the absence of CO₂ in O₂. This improved conversion was connected to the production of per-oxycarbonate groups over the catalyst surface. Furthermore, in the existence of CO₂, the secondary reactions also emerged more remarkable, possibly due to the acidity of the CO₂ molecules adsorbed onto the DBH matrix. In comparison with O₂ alone, the conversion of *p*-xylene was higher in the co-presence of CO₂ at all temperatures (Figure 2). The O₂/N₂/CO₂ feed system, resulted in a higher conversion of *p*-xylene and greater selectivity towards benzaldehyde at temperatures from 300 °C to 375 °C (Table 4). It was observed that no carbon dioxide was formed by the burning of *p*-xylene over the catalyst at 375 °C; however, in the O₂/N₂/He feed system, the formation of CO₂ started (10.7%) at 300 °C and significantly increased (20.2%) at 375 °C. Thus, CO₂ performed as a co-oxidant for the gas-phase *p*-xylene oxidation reaction with oxygen. Yoo et al. [20] also reported a significant enhancement in the conversion of *p*-xylene, *p*-ethyl toluene, and *o*-xylene in the presence of CO₂ at varying temperatures.

Table 3. Effect of CO₂ on the MC-type catalyst for oxidation of *p*-xylene (Reproduced from [22]; copyright (2012), Royal Society of Chemistry).


| Gas | Conversion of 1 (%) | Yield mol (%) | | | | |
|---------------------------------|---------------------|---------------|------|-----|-----|------|
| | | 2 | 3 | 4 | 5 | 6 |
| O ₂ | 57.2 | 17.7 | 47.9 | 2.8 | 1.7 | 29.2 |
| O ₂ /CO ₂ | 66.8 | 34.8 | 36.9 | 1.7 | 2.4 | 24.2 |

Reaction conditions: Temperature 170 °C, time 3 h, Mesoporus carbon (MC) type catalyst with transition metal additive (Co/Mn/Br), Co 100 ppm, Mn 200 ppm, Br 300 ppm [38].

**Figure 2.** Promotional role of CO₂ on Fe/Mo/DBH for the oxidation of *p*-xylene.**Table 4.** Enhance effect of CO₂ on oxidation of *p*-xylene (Reproduced from [20]; copyright (1993), Elsevier). Reaction conditions: WHSV: 0.22 h⁻¹, contact time: 0.21 s, gas flowrate: 400 sccm, Feed gas 1: 0.1% *p*-xylene, 1% O₂, 1% N₂ in He. Feed gas 2: 0.1% *p*-xylene, 1% O₂, 1% N₂ in commercial grade CO₂.

| Temperature (°C) Feed ^a | 300 | | 350 | | 375 | |
|------------------------------------|------|------|------|------|------|------|
| | 1 | 2 | 1 | 2 | 1 | 2 |
| <i>p</i> -Xylene (Con.%) | 17.6 | 33.3 | 41.2 | 65.5 | 60.7 | 84.1 |
| Product selectivity (mol%) | - | - | - | - | - | - |
| <i>p</i> -Tolu-aldehyde | 57.9 | 57.2 | 50.2 | 40.9 | 40.6 | 40.6 |
| Terephthalaldehyde | 16.4 | 27.5 | 23.5 | 33.6 | 32.6 | 30.2 |
| Benzaldehyde | 1.3 | 1.5 | 2.4 | 2.7 | 2.7 | 3.1 |
| Maleic anhydride | 0.0 | 0.0 | 2.4 | 6.0 | 5.8 | 13.7 |
| Toluene | 6.2 | 6.9 | 3.5 | 4.8 | 3.1 | 4.8 |
| Trimethyl biphenyl methane | 7.5 | 6.8 | 1.7 | 0.6 | 0.4 | 0.0 |
| CO | 0.0 | 0.0 | 0.6 | 3.4 | 4.7 | 7.5 |
| CO ₂ | 10.7 | 0.0 | 15.6 | 0.0 | 20.2 | 0.0 |

^a Feed gas 1: O₂/N₂/He, Feed gas 2: O₂/N₂/CO₂.

2.4. Oxidation of *p*-Toluic Acid and *p*-Methyl-Anisole

CO₂ acts as a promoter in catalytic systems and as a co-oxidant with O₂ resulting in improved reaction kinetics, more desirable product distributions, better selectivity, and higher conversion. Initially, Aresta et al. [32] reported that carbon dioxide enhanced the oxidative characteristics of dioxide in transition metal systems. Park et al. [38] studied the use of Co/Mn/Br catalysts in the fluid-phase oxidation of olefins. Interestingly, they observed the expansion effect of carbon dioxide on mesoporous carbon nitride (MCN) catalytic systems, whereas the CO₂-promoted system was fabricated by them on the oxidation of alkyl-aromatics. In the presence of CO₂, the conversion of *p*-toluic acid over the metal carbonate (MC) catalyst was increased by 12% (Table 5) compared to oxidation in O₂ alone. Furthermore, the yield of terephthalic acid increased from 58.2% to 64.9%. These data demonstrate that the catalytic activity is significantly enhanced by CO₂. Interestingly, over an MC-supported catalytic system, the main product of the oxidation of *p*-methyl-anisole is *p*-methoxy phenol (Table 6) along with a limited number of other products, such as *p*-anisaldehyde and *p*-anisic acid. However, the yield of *p*-anisaldehyde has increased the presence of CO₂, again demonstrating the capacity of CO₂ to sustain mono-oxygen transfer.

Table 5. *p*-toluic acid oxidation with CO₂ on an MC-type catalyst (Reproduced from [22]; copyright (2012), Royal Society of Chemistry).

| Gas | Conversion of 1 (%) | Yield mol (%) | |
|---------------------------------|---------------------|---------------|------|
| | | 2 | 3 |
| O ₂ | 60.9 | 58.2 | 3.7 |
| O ₂ /CO ₂ | 72.7 | 64.9 | 10.6 |

Reaction conditions: 6 mL *p*-toluic acid, 0.1183 g CoBr₂, 0.1587 g Mn(OAc)₂·4H₂O in 24 mL HOAc, temperature 190 °C, time 3 h; P_{CO₂} = 0.6 atm, P_{O₂} = 2 atm [38].

Table 6. Performance of CO₂ on oxidation of *p*-methylanisole (Reproduced from [22]; copyright (2012), Royal Society of Chemistry).

| Gas | Conversion of 1 (%) | Yield mol (%) | | |
|---------------------------------|---------------------|---------------|------|----|
| | | 2 | 3 | 4 |
| O ₂ | 94.9 | 2.05 | 0.83 | 92 |
| O ₂ /CO ₂ | 98 | 7.7 | 0.38 | 90 |

Reaction conditions: 43.5 mmol *p*-methylanisole, 0.6 mmol CoBr₂, 0.6 mmol Co(OAc)₂, 0.6 mmol Mn(OAc)₂·4H₂O in 30 g HOAc, total pressure 12 atm (P_{CO₂} = 0.2 atm, P_{O₂} = 2,3,6 atm, P_{N₂} balance). temperature 120 °C, time 3 h [38].

3. Performance of CO₂ in Oxidative Dehydrogenation

3.1. Influence of CO₂ on Dehydrogenation of Ethyl Benzene

Styrene is typically formed by the dehydrogenation of ethyl benzene under the steam on a metal oxide catalyst in an adiabatic reactor [39]. There are several limitations to this process, including thermodynamic drawbacks, low conversion rates, high endothermic energy ($\Delta H^{\circ}_{298} = 123.6 \text{ kJ mol}^{-1}$), huge energy destruction, and catalyst deactivation by coke production [40]. An alternative method of styrene production is the oxidative dehydrogenation reaction with O₂; however, this results in the burning of large quantities of valuable hydrocarbons. In this context, the use of CO₂ in the oxidative dehydrogenation of ethyl benzene may prove useful [39–61]. Zhang et al. [43] confirmed coke deposition using spectroscopy and reported the deactivation of a ceria catalyst without CO₂ present. In a two-step, reaction mechanism for the dehydrogenation of ethyl benzene to produce styrene with H₂ in the initial step and in the presence of CO₂, ejection of H₂ through a reverse water-gas shift (RWGS) reaction was also demonstrated [41]. Kovacevic et al. revealed the results of CeO₂ catalyst morphology (i.e., rods vs. cubes vs. particles) in the presence and absence of CO₂ [42]. They reported that in the presence of CO₂ cubic catalysts showed higher initial benzene selectivity, and about two times more activity per m² compared to the reaction without CO₂. Interestingly, the number of oxygen species was increased by the presence of CO₂. They also observed that these additional oxygen molecules were expended in the ethyl benzene conversion, demonstrating their performance as active sites for styrene formation. Periyasamy et al. reported that in the ODH reaction the conversion of ethyl benzene (EB) was 50% and the selectivity for styrene was 93% at gas hourly space velocity (GHSV) 2400 h⁻¹. They also observed that the conversion and selectivity increased with enhancing oxidant flow ratio, up to GHSV 2400 h⁻¹.

Park et al. [49] reported on the use of SBA-15 as a beneficial backing for a ceria-zirconium (25:75) combined oxide catalyst for oxidative dehydrogenation of ethyl benzene utilizing carbon dioxide. Ce-Mn oxide nanoparticles enclosed inside carbon nanotubes (CNTs) were used for the oxidative dehydrogenation of ethyl benzene with CO₂ acting as a soft oxidant. The high diffusion and the encapsulation effect of CNTs resulted in excellent performance of the entrapped catalysts. Correlated to CeO₂ support CNTs, the restriction result of CNT pathways enhanced the communication between carbon nanotube (CNT) inner walls and CeO₂ particles, which is orderly, convinced the misrepresentation of CeO₂ crystal lattice which is advertised CeO₂ reduction and invigoration of CeO₂ surface lattice oxygen. The unique process of promoting oxidative catalytic activity the addition of CO₂ was reported by Zhang et al. [44]. They observed that multi-walled carbon nanotubes (MWCNTs) have a significant quantity of surface hydroxyl groups which are produced by an alkali-supported hydrothermal method after ball milling. The MWCNTs can mostly arrange the active sites for the oxidative dehydrogenation of ethyl benzene (EB) in the existence of CO₂. Figure 3a shows the conversion of ethyl benzene over various types of MWCNTs at 3 hr. The HMWCNTs-OH exhibits significant catalytic activity, indicating that the surface hydroxyl groups are the active sites for the oxidative dehydrogenation of ethyl benzene. The O1s spectra of HMWCNTs-B-OH identified by XPS is shown in Figure 3b. Figure 3c demonstrates the production of carbonyl groups in the reaction. The results indicate that CO₂ acts effectively as a soft oxidant, directly oxidizing -OH groups into carbonyl groups. As shown in Figure 3d, CO and H₂ were also identified as byproducts for the reaction, indicating that CO₂ is reduced in the RWGS reaction. CO₂ activation occurs via electron donation from the surface of the catalyst to the anti-bonding orbital of CO₂ [62]. However, ethyl benzene (EB) can be activated for oxidative dehydrogenation (ODH) by donating an electron to the acidic portion of the catalyst surface.

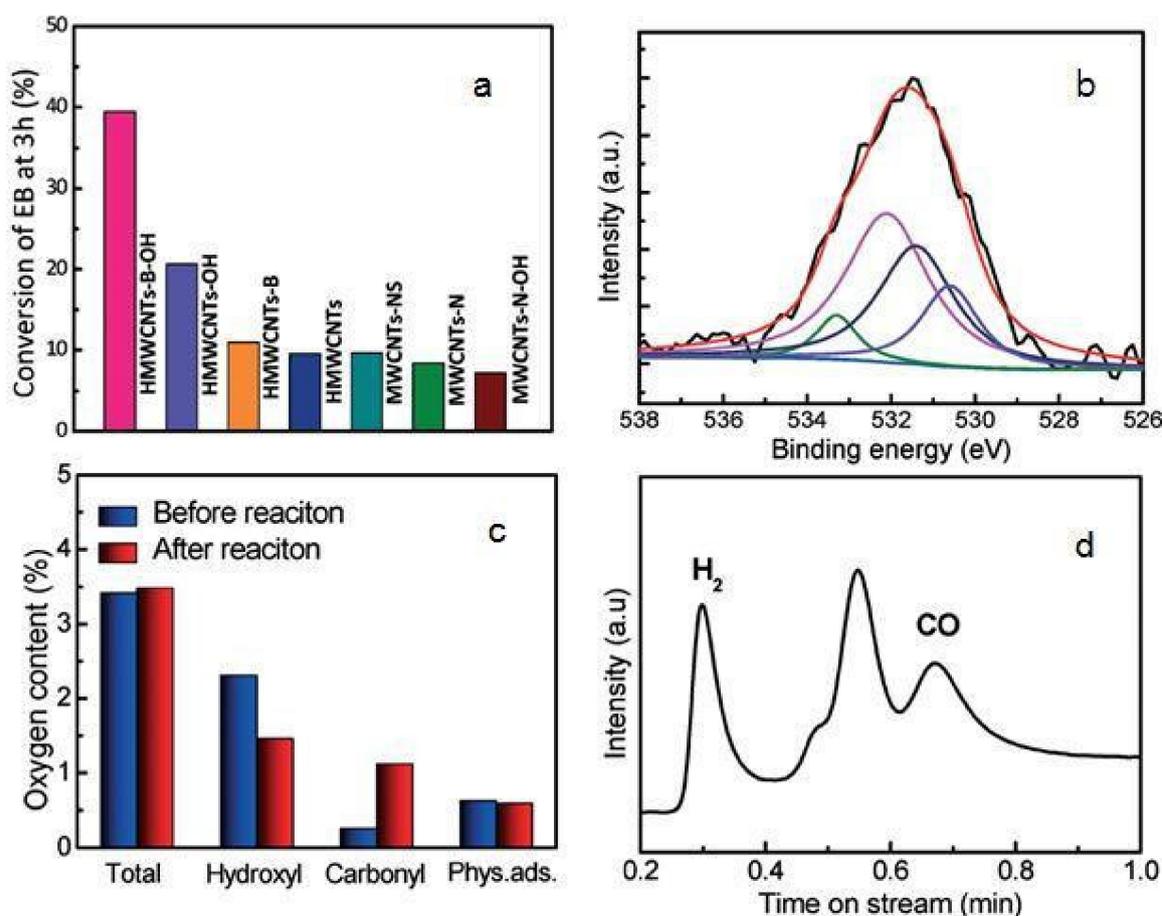


Figure 3. (a) Conversion of EB using CO₂ as a soft oxidant; (b) O1s spectra of HMWCNTs-B-OH after oxidative dehydrogenation by XPS for 3 hr; (c) Oxygen substance (mol%) of HMWCNTs-B-OH earlier and later oxidative dehydrogenation reaction at 3 h; (d) Gas derivatives of HMWCNTs-B-OH after oxidative dehydrogenation at 3 h. (Reprinted from [44]; copyright (2013), Royal Society of Chemistry).

Additionally, basic sites abstract hydrogen from ethyl benzene. Thus, the aggregated effect of the basic and acidic sites of the catalyst face is the oxidative dehydrogenation reaction, resulting in high catalytic efficiency in the existence of CO₂ [63]. Sato et al. reported on the use of CO₂ as a mild oxidant in the oxidative dehydrogenation reaction as well as the typical dehydrogenation process in the absence of CO₂. Two mechanisms utilizing acidic and basic sites were proposed, as depicted in Figure 4. Vanadium-embed catalysts also used in CO₂ based oxidative dehydrogenation of oxidative dehydrogenation of ethyl benzene (ODHEB) reactions [21,45]. CO₂, being a mild oxidant, cannot reproduce the active sites on the V₂O₅ (001) surface of the catalyst quickly enough due to the large activation energy (3.16 eV) [46]. A ceria-supported vanadium catalyst floated on a titania-zirconia combined oxide (TiO₂-ZrO₂) has moderate constancy which was reported by Reddy et al. [47]. XPS analysis of Ce 3d indicated the presence of Ce⁴⁺ and Ce³⁺ on the Ti-Zr catalyst. They also reported that CeO₂-V₂O₅/TiO₂-ZrO₂ (TZ) catalysts resulted in 56% conversion of ethylbenzene and 98% selectivity of styrene. Liu et al. [48] illustrated the red-ox mechanism for the CO₂-oxidative dehydrogenation of ethyl benzene (CO₂-ODEB) using a ceria promoted vanadium catalyst, as shown in Figure 5. In the CO₂-ODEB case, CO₂ directly oxidizes Ce³⁺ to Ce⁴⁺, and ethylbenzene reduces of V⁵⁺ to V⁴⁺. Then, the reduction of Ce⁴⁺ to Ce³⁺ and the oxidation of V⁴⁺ to V⁵⁺ completes the full cycle. In the existence of CO₂, modified vanadium catalysts are effective, selective, and stable for the ODEB, as reported by Park et al. [49] Rapid regeneration of active sites on a silica-assisted vanadium catalyst along in the presence of CO₂ has also been reported [64]. 10% La₂O₃-15%V₂O₅/SBA-15 (wt.%)

catalyst resulted in a 74% styrene yield, with La^{3+} resisting coke ejection [50]. The use of supporting materials, such as Aluminum mesoporous cylindrical molecular sieve (Al MCM-41) also resulted in substantial EB conversion in the ODEB using a $\text{VO}_x/\text{Al MCM-41}$ catalyst in the presence of CO_2 [51]. ZrO_2 -containing combined oxide catalysts for oxidative dehydrogenation of ethylbenzene with CO_2 in the presence of MnO_2 , CeO_2 and TiO_2 have exhibited high activity. The styrene yield was also increased over the MnO_2 - ZrO_2 dual oxide catalyst at a high temperature. Significant enhancement of catalytic activity was checked with increasing CO_2/EB ratios [52]. A TiO_2 - ZrO_2 catalyst was used, and the proportion of $\text{TiO}_2/\text{ZrO}_2$ determined the catalytic activity [53–55,65]. A 60% titania content resulted the best performance for the ODEB [65,66]. Commercial Fe-supported catalysts are unsuitable for the oxidative dehydrogenation of ethyl benzene in the existence of carbon dioxide due to the atomization of the active catalytic site [56]. However, the use of appropriate dopants' support materials might enhance the activity by promoting re-oxidation of Fe^{2+} and preventing coke deposition [57,58]. High product yield stability was observed in a mesoporous silica COK12-assisted CoO_3 catalyst [59]. The performance of several effective catalysts in the oxidative dehydrogenation of ethyl benzene to styrene in the existence of CO_2 is shown in Table 7.

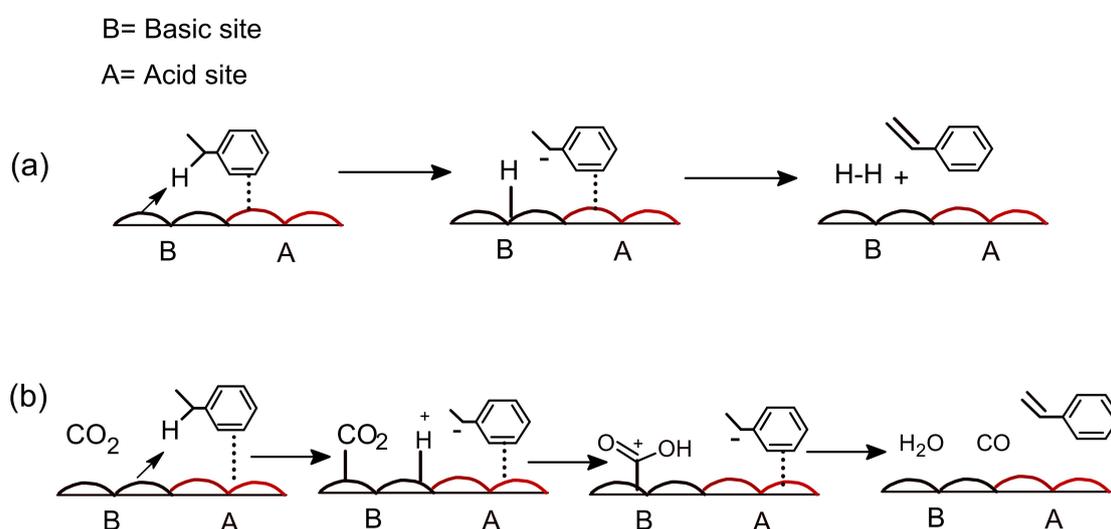


Figure 4. The procedure of oxidative dehydrogenation of ethylbenzene to styrene (a) without CO_2 and (b) with CO_2 . (Reproduced with permission from [62]; copyright (2016), Elsevier).

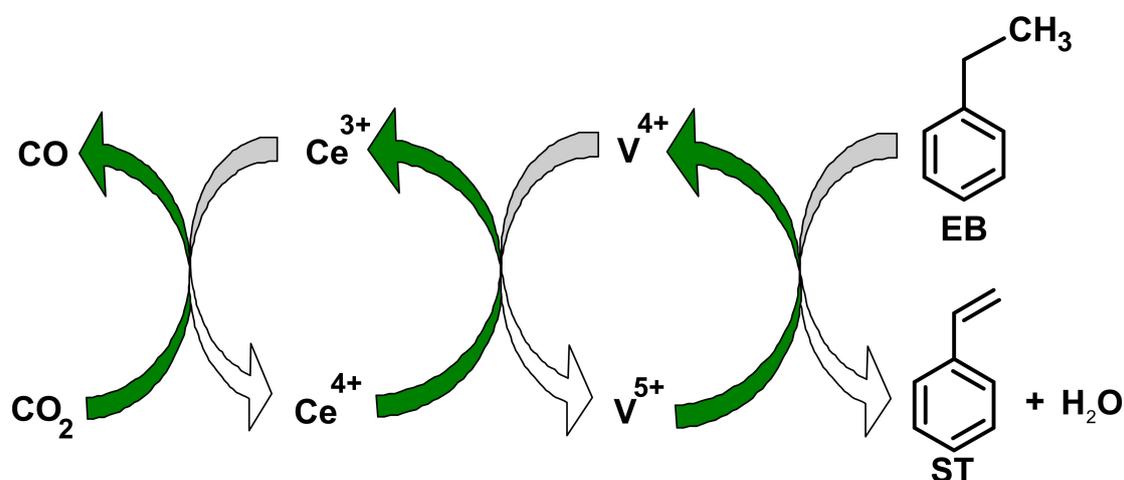


Figure 5. Red-ox cycle for CO_2 -ODEB over the ceria-promoted vanadium catalyst. (Reproduced from [48]; copyright (2011), WILEY-VCH).

Table 7. Performance of CO₂ on oxidative dehydrogenation of ethylbenzene to styrene.

| Catalyst | Reaction Temperature (°C) | EB Conversion (%) | ST Selectivity (%) | ST Yield (%) | Ref. |
|---|---------------------------|-------------------|--------------------|--------------|------|
| Co ₃ O ₄ /COK-12 | 600 | 57.5 | 95.5 | 54.9 | [59] |
| CeZrO _{4-δ} | 550 | 7 | 97 | 6.8 | [61] |
| Na X zeolite | 545 | 9.4 | 89.6 | 8.4 | [60] |
| K X zeolite | 545 | 10.5 | 92.1 | 9.6 | [60] |
| VO _x /Al MCM-41 | 550 | 52.3 | 96.7 | 50.6 | [51] |
| TiO ₂ -ZrO ₂ | 600 | 69.3 | 96.2 | 66.6 | [67] |
| V ₂ O ₅ /SiO ₂ | 550 | 50.5 | 96.8 | 48.8 | [64] |
| SnO ₂ -ZrO ₂ | 600 | 61.1 | 97.6 | 59.6 | [68] |
| MnO ₂ -ZrO ₂ | 600 | 51.1 | 99.1 | 50.9 | [69] |

3.2. Performance of CO₂ on Dehydrogenation of Ethane

Ethylene is one of the most prominent raw materials in the chemical industry. Presently, it is used to produce industrial products such as PVC, ethylene glycol, ethylbenzene, ethylene oxide, and vinyl acetate. Commercially, ethylene is formed by steam cracking dehydrogenation of hydrocarbons and fluid catalytic cracking (FCC). These conventional methods have several major limitations including the reaction endothermicity, thermodynamic drawbacks, rapid coke formation, and high energy consumption. The oxidative dehydrogenation of ethane (ODHE) to ethylene in the presence of CO₂ as a mild oxidant is an environmentally friendly alternative method for the production of ethylene. A Cr-oxide catalyst with zeolite support was successfully used for the oxidative dehydrogenation of ethane in the presence of CO₂ as a soft oxidant. A novel Clinoptilolite-based Cr-oxide (Cr/CLT-IA) catalyst for the ODHE in the existence of CO₂ was investigated by Rahamani et al. [70]. This Cr-supported catalyst exhibits high selectivity and catalytic activity which was expected due to its acidity. Homogeneous, tunable smaller Clinoptilolite-based Cr catalyst particles with higher surface area can be generated. Thus, using a Cr/CLT-IA nano-catalyst may be feasible and favorable for the oxidative dehydrogenation of ethane to ethylene in the existence of CO₂. Cr/H-ZSM-5 (SiO₂/Al₂O₃ ≥ 190) outperformed the SiO₂-based catalyst in the oxidative dehydrogenation of ethane to ethylene with CO₂ [71]. CO₂ is a promising soft oxidant for the ODHE reaction acting as a channel for transporting heat to the endothermic dehydrogenation. Further, CO₂ improves the conversion by modifying alkanes and maintains the catalytic activity by eliminating coke from the catalyst surface. The texture of the Cr active sites and the catalyst activity are determined by the SiO₂/Al₂O₃ ratio. The presence of more alumina amount in the zeolite negatively affected the activity of the catalyst, due to the incorporation of alumina with the Cr into the catalyst structure, affecting the red-ox properties of Cr. Mimura et al. [71] reported on the dehydrogenation of ethane on a Cr-doped HZSM-5 catalyst which is established on the redox phase of the eminent oxidation type Cr species. In their work, C₂H₆ was absorbed on the acidic site of CrO_x and H-ZSM-5. Then, the activated C₂H₆ reacted with CrO_x (active O species) to produce ethylene. The CrO_{x-1} species is then re-oxidized by the soft oxidant CO₂ regenerating the active O species and eliminating coke from the surface of the catalyst. The catalytic performance of the Cr-supported mesoporous catalyst, as well as a Cr-doped silicate MSU-1 catalyst, in the ethane oxidative dehydrogenation to ethylene in the presence of CO₂ was reported on by Liu et al. [72]. They initially observed high catalytic activity due to the Cr(VI) active species. However, even in the existence of CO₂, the reduction of Cr(VI) to Cr(III) occurred, resulting in the deactivation of the catalyst during the dehydrogenation reaction. Shi et al. [73] reported that Cr-supported Ce/SBA-15 catalysts were comprised of hexagonally ordered mesoporous frameworks and exhibited high catalytic activity in the oxidative dehydrogenation of ethane in the existence of CO₂. They confirmed the addition of Ce species using high-angle XRD, which increased the Cr species distribution in the Cr-Ce based SBA-15 zeolite. TPR results determined that Cr species in SBA-15-type zeolites are Cr⁶⁺ and Cr³⁺ groups. Among those two ions, Cr⁶⁺ exhibited significant activity for the oxidative dehydrogenation reaction in the existence of CO₂. Including a Ce-supported in 5Cr/SBA-15 catalysts modified the red-ox properties and enhanced the activity of the catalyst. Ethane conversion was 55% and ethylene

selectivity was 96% on the 5Cr-10Ce/SBA-15 catalyst in the existence of CO₂ (Table 8). Cr⁶⁺ is reduced to Cr³⁺ during the oxidative dehydrogenation method reaction, however, in the presence of CO₂, Cr³⁺ is re-oxidized to Cr⁶⁺. Cr₂O₃/ZrO₂ supported catalysts with Fe, Co, Mn was also investigated in an effort to fully understand the excellent catalytic activity for the ethane dehydrogenation reaction to ethylene under CO₂ treatment [64,65,74]. The Cr⁶⁺/Cr³⁺ red-ox cycle is crucial in the oxidative dehydrogenation reaction, as is a Fe³⁺/Fe²⁺ red-ox cycle which removes H₂ from the lattice oxygen. An SBA-15-based, Cr-modified catalyst using a Fe-Cr-Al alloy [75] also exhibited remarkable selectivity of ethylene and high ethane conversion in the oxidative dehydrogenation reaction with CO₂. Wang et al. [64] observed the red-ox properties and the acidity/basicity of the Cr-supported catalyst in the oxidative dehydrogenation of ethane to ethylene with CO₂. They found that Cr-supported catalysts exhibited different activities in the ODHE with CO₂. Cr₂O₃/SiO₂ showed higher ethane conversion and ethylene selectivity. The catalytic activities were ranked as follows Cr/SiO₂ > Cr/ZrO₂ > Cr/Al₂O₃ > Cr/TiO₂ [76,77]. Notably, Cr₂O₃ interacted more with Al₂O₃ than with SiO₂, resulting in tetrahedral Cr⁶⁺ sites and declining activity [78]. Cr is one of the vital elements of various types of nano-catalysts (Table 9). The active site of these catalysts contains both Cr³⁺ and Cr⁶⁺. The Cr⁶⁺/Cr³⁺ ratio strongly influences the reducibility of Cr/H-ZSM-5 catalysts. The red-ox performance of Cr-supported catalysts is crucial for the oxidative dehydrogenation of ethane to ethylene in the presence of CO₂ as a soft oxidant. Cr⁶⁺ (or Cr⁵⁺) sites are reduced to Cr³⁺ as ethane is dehydrogenated. Then, the reduced Cr³⁺ sites are re-oxidized by carbon dioxide treatment. Mimura et al. reported that the highly active Cr-based catalysts had Cr⁶⁺ or Cr⁵⁺ species on the surface of the catalyst [79]. Apart from Cr-supported catalysts, several other effective catalysts have been used in research on ethane oxidative dehydrogenation. Among these, the Ni-Nb-mixed oxide catalyst performed very well at relatively low temperatures [80–82]. Additionally, a TiO₂-based Ga catalyst proved applicable for oxidative dehydrogenation with CO₂ [83].

Table 8. Catalytic activity for the dehydrogenation of ethane (Reproduced from [73]; copyright (2008), Springer (Berlin, Germany)).

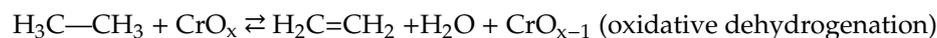
| Catalyst | In the Presence of CO ₂ | | | | In the Presence of Ar | | |
|------------------|------------------------------------|-----------------|-------------------------------|-----------------|-----------------------|-------------------------------|-------------------------------|
| | Conv. (%) | | Selectivity (%) | | Conv. (%) | Selectivity (%) | |
| | C ₂ H ₆ | CO ₂ | C ₂ H ₄ | CH ₄ | | C ₂ H ₆ | C ₂ H ₄ |
| SBA-15 | 2.7 | 0.04 | 93.5 | 6.5 | 2.4 | 93.0 | 7.0 |
| 2.5Cr/SBA-15 | 39.6 | 15.9 | 95.5 | 4.5 | 30.2 | 89.7 | 10.3 |
| 5.0Cr/SBA-15 | 46.3 | 16.6 | 94.7 | 5.3 | 34.1 | 91.4 | 8.6 |
| 7.5Cr/SBA-15 | 45.3 | 18.8 | 92.2 | 7.8 | 33.9 | 92.8 | 7.2 |
| 10Cr/SBA-15 | 44.2 | 18.9 | 92.0 | 8.0 | 31.2 | 90.9 | 9.1 |
| 5Cr-5Ce/SBA-15 | 48.4 | 17.9 | 96.4 | 4.6 | 35.8 | 87.6 | 12.4 |
| 5Cr-7.5Ce/SBA-15 | 50.0 | 20.9 | 96.0 | 4.0 | 37.9 | 88.2 | 11.8 |
| 5Cr-10Ce/SBA-15 | 55.0 | 21.9 | 96.0 | 4.0 | 40.8 | 83.1 | 16.9 |
| 5Cr-15Ce/SBA-15 | 52.2 | 21.2 | 95.5 | 4.5 | 40.1 | 82.4 | 17.6 |

Reaction conditions: GHSV = 3600 mL/g h, T = 700 °C.

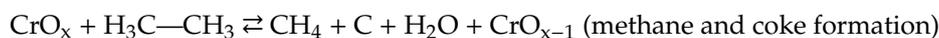
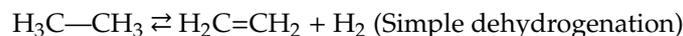
Table 9. Influence of CO₂ on oxidative dehydrogenation of ethane.

| Catalyst | Ethane Conversion (%) | Ethylene Selectivity (%) | Ethylene Yield (%) | Ref. |
|--|-----------------------|--------------------------|--------------------|------|
| Cr ₂ O ₃ (5 wt.%) CLT-IA | 39.7 | 98.8 | 39.2 | [70] |
| 3Cr/NaZSM-5-160 | 65.5 | 75.4 | 49.3 | [84] |
| Cr ₂ O ₃ /Al ₂ O ₃ -ZrO ₂ | 36.0 | 56.2 | 20.2 | [85] |
| Cr/MSU-1 | 68.1 | 81.6 | 55.6 | [72] |
| Cr ₂ O ₃ /ZrO ₂ | 77.4 | 46.3 | 35.8 | [86] |
| 2.5 Cr/SBA-15 | 46.3 | 94.7 | 43.8 | [75] |
| 5 Cr-10Ce/SBA-15 | 55.0 | 96.0 | 52.8 | [73] |
| 5% Cr ₂ O ₃ /Al ₂ O ₃ | 19.2 | 56.5 | 10.8 | [77] |

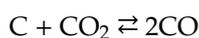
Step-1



Step-2



Step-3



3.3. Influence of CO₂ on the Alkylation of Toluene Side-Chain

The dehydrogenation of ethylbenzene produces the most styrene using the Friedel-Crafts alkylation reaction [87]. However, the ethylbenzene dehydrogenation method has some limitations such as catalyst deactivation and, high energy consumption [88,89]. Alkylation of the toluene side-chain is a promising alternative process that uses basic catalysts for the formation of styrene in the existence of CO₂. Another process was reported by Sindorenko et al. [90] utilizing K⁺ and Rb⁺ ion transposing Faujasite supported catalysts in 1967. However, the catalytic conversion of toluene and styrene monomer (SM) selectivity was low (Table 10) [91]. The side-chain alkylation is primarily carried out on solid base catalysts [92–96]. Toluene side-chain alkylation with methanol enhanced by the promotional use of alkali metal oxides. Greater catalyst acidity accelerates methanol dehydration, [97] while low concentrations of alkali metal ions prevent the decomposition of formaldehyde produced from methanol [98]. Thus, catalysts for this reaction must be optimized for their acidity and basicity [99]. Generally, catalyst sites for the side-chain alkylation are limited to alkali metal-altered zeolites [100]. One reliable, widely studied catalyst is the cesium ion-exchanged or Ce₂O-impregnated zeolite-X. The advantages of a MgO-supported mesoporous catalyst for this reaction has also been reported by Park et al. [101]. Hattori et al. observed that the impregnation of Cs₂O in ion-exchanged zeolite-X results in high conversion of toluene, owing to the strongly basic sites [102]. Carbon dioxide has been under consideration as a renewable, low-cost, safe, and environmentally beneficial feedstock in current years. CO₂ utilization is difficult for commercial applications, owing to its high thermal stability as well as the solid oxidation phase [103]. Hence, remarkable research efforts are being directed to detect innovative technologies for the utilization of CO₂. Toluene side-chain alkylation was performed to assess the efficacy of the catalytic approach with methanol over cesium-supported catalysts. Toluene and methanol conversion over the Cs-X and Cs-modified zeolites in the presence of He and CO₂ are shown in Table 10. In these reactions, styrene and ethylbenzene were formed as main products. Other side-chain alkylated components, including cumen and α-methyl styrene, as well as other xylenes, tri-methylbenzene, and benzene were identified as by-products. When the catalytic reaction was carried out in the existence of CO₂, methanol and toluene conversion increased. Though the styrene selectivity decreased, there was a significant increase in the conversion as well as product selectivity in the presence of He and CO₂ streams. TG/DTA analysis of the used Cs-X catalyst in the presence of CO₂ and He streams is shown in Figure 6. In the range of 25–200 °C, weight loss occurred owing to the desorption of adsorbed water [94]. The continued weight loss in the 200–450 °C region occurred due to the deposition of coke on the surface of the catalyst. Relatively high quantities of coke were deposited on the Cs-X catalyst in the existence of the CO₂. This suggests greater deactivation of the catalyst in the presence of carbon dioxide owing to coke deposition [89]. Still the Cesium-supported catalysts performed better in the presence of CO₂ than under He in terms of toluene and methanol conversion. CO₂ acted as a significant performance in hydrogen skulking and enhanced the reaction

rate in the decisive route. Additionally, CO₂ increases alkylation to produce cumin and α -methyl styrene, which are side-chain alkylation products. Further, the increased toluene conversion enhances the aromatic yields.

Table 10. Performance of CO₂ in the toluene side-chain alkylation (Reproduced with permission from [91]; copyright (2018), Elsevier).

| Catalyst | Carrier Gas | MeOH Conv. (%) | Toluene Conv. (%) | Selectivity (%) | | |
|----------------------------|-----------------|----------------|-------------------|-----------------|-------|--------|
| | | | | SM | EB | Others |
| Ce-X | He | 12.54 | 1.42 | 78.61 | 15.32 | 6.07 |
| | CO ₂ | 35.35 | 3.48 | 45.83 | 33.36 | 20.81 |
| Cs ₂ O/ Cs-X | He | 46.48 | 3.59 | 28.76 | 68.02 | 3.22 |
| | CO ₂ | 39.16 | 2.52 | 36.02 | 43.02 | 20.78 |

Reaction conditions: WHSV = 2.1 h⁻¹, Reaction temperature = 425 °C, Toluene/MeOH molar ratio = 2, SM = Styrene Monomer and other byproducts = Cumene, Xylenes, TMB and Benzene.

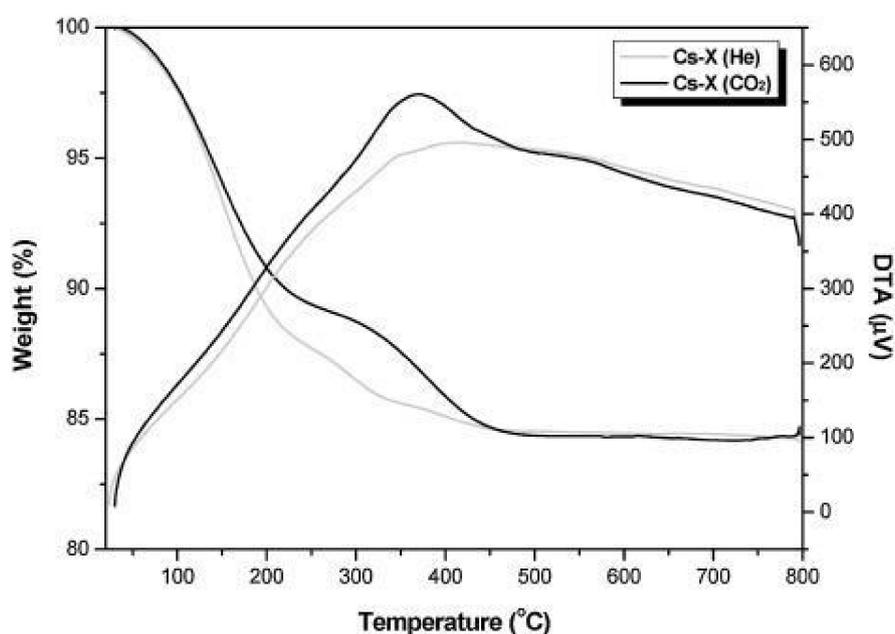


Figure 6. TG/DTA results obtained for used Cs-X catalyst in the presence of CO₂ and He streams (Redrawn with permission from [91]; copyright (2018), Elsevier).

3.4. Role of CO₂ on Dehydrogenation of Propane

Propylene is the most prominent raw material in the chemical industries. It is primarily manufactured by steam cracking and propane oxidative dehydrogenation [104–106]. Oxidative dehydrogenation (ODH) is preferred due to its low energy requirements and lack of thermodynamic limitations [107,108]. However, the ODH reaction with O₂ occurs under potentially flammable conditions and forms of carbon oxides due to over-oxidation with low selectivity [109,110]. This complication can be resolved using CO₂ as a mild, safer oxidant. Thus, this reaction is a favorable example of CO₂ utilization. Interestingly, CO₂ was used as a mild oxidant to shift the equilibrium more toward the products, as well as enhance the dehydrogenation over the coupling between propane oxidative dehydrogenation to propylene and the reverse water gas shift (RWGS) reaction [111–113]. Dehydrogenation of propane occurred on the acid site of the catalyst. The SiO₂/Al₂O₃ proportion is critical in determining both the catalyst physicochemical properties and its reactivity characteristics [114–117]. The HZSM-5, SBA-15, MCM-41, SBA-1 catalyst which is a two-dimensional microchannel system, has been used in the oxidative dehydrogenation of alkanes especially for the conversion of methane to propane in the existence of CO₂. Various research groups have reported

on the influence of catalyst acidity in the oxidative dehydrogenation reaction with CO₂. The activity of the zeolites decreased with increasing Si/Al proportion in HZSM-5 based Ga₂O₃, although the selectivity increased, as shown in Figure 7 [118]. Lewis acidity is present in the metal oxide (Ga₂O₃) catalyst, while Bronsted acidity is present in HZSM-5. Thus, extracting the aluminum from HZSM-5 declines the Bronsted acidity more than it decreases the Lewis acidity. Several transition metals, such as vanadium, molybdenum, and chromium, have been used to support catalysts for ODH of light alkanes including propane [105,112,119,120]. Among these, chromium oxide provided high catalytic performance with CO₂, despite fractional deactivation by coke production. Chromium oxide enhanced propane conversion and the propylene selectivity by expelling H₂ produced in the ODH reaction [112]. The catalytic performance of Cr-supported catalysts was observed by the character of chromium categories on the support surface of the catalysts [121–125]. Park et al. found that different Cr doping of Cr-TUD-1 catalysts (3, 5, 7 and 9 wt.%) with soft oxidant (CO₂) were formed by MW irradiation and investigated the propane oxidative dehydrogenation [126]. The effect of reaction temperature on the oxidative dehydrogenation of propane in the existence of CO₂ as a mild oxidant over the Cr-TUD-1 catalyst (7 wt.%) was investigated thoroughly to improve the catalytic activity. The conversion of CO₂ was 3.5% at 550 °C and improved to 5.5% at 650 °C. To demonstrate the importance of CO₂ in the propane oxidative dehydrogenation on Cr-TUD-1 catalysts, the process was carried out at 550 °C on 7 wt.% catalyst under the same conditions in the presence of CO₂ as well as He. The decline in the catalytic activity of the catalyst with helium may be due to coke production and the reduction of the Cr groups on the surface of the zeolite. The proposed mechanism of propane oxidative dehydrogenation over metal oxide surfaces with the CO₂ stream is shown below [112]:

A weak exclusive propane adsorption on the lattice oxygen



C-H schism via H-abstraction from propane utilizing an abutting lattice oxygen



Propylene desorption by hybrid expulsion from adsorbed alkoxide groups



Reconsolidation of OH groups to produce H₂O, reduced metal center (*)



Re-oxidation of abridged M-centers by separating chemisorptions of CO₂



To evaluate the deactivation of the catalyst by coke creation and the enhancement of CO₂, (Equation (7)) can be used as the deactivation parameter:

$$\text{Deactivation parameter (\%)} = \frac{\text{Conversion of propane (initial amount - final amount)}}{(\text{initial amount}) * 100} \quad (7)$$

The rate of Cr degradation by H₂ liberated from dehydrogenation is faster than the rate at which CO₂ re-oxidizes the degraded Cr species, resulting in catalytic deactivation. Selective adsorption properties can be improved by surface functional groups on activated carbons. Thus, surface treatment of activated carbon may result in more selective and efficient adsorption of the gas, liquid and the alleviation of pollution [127].

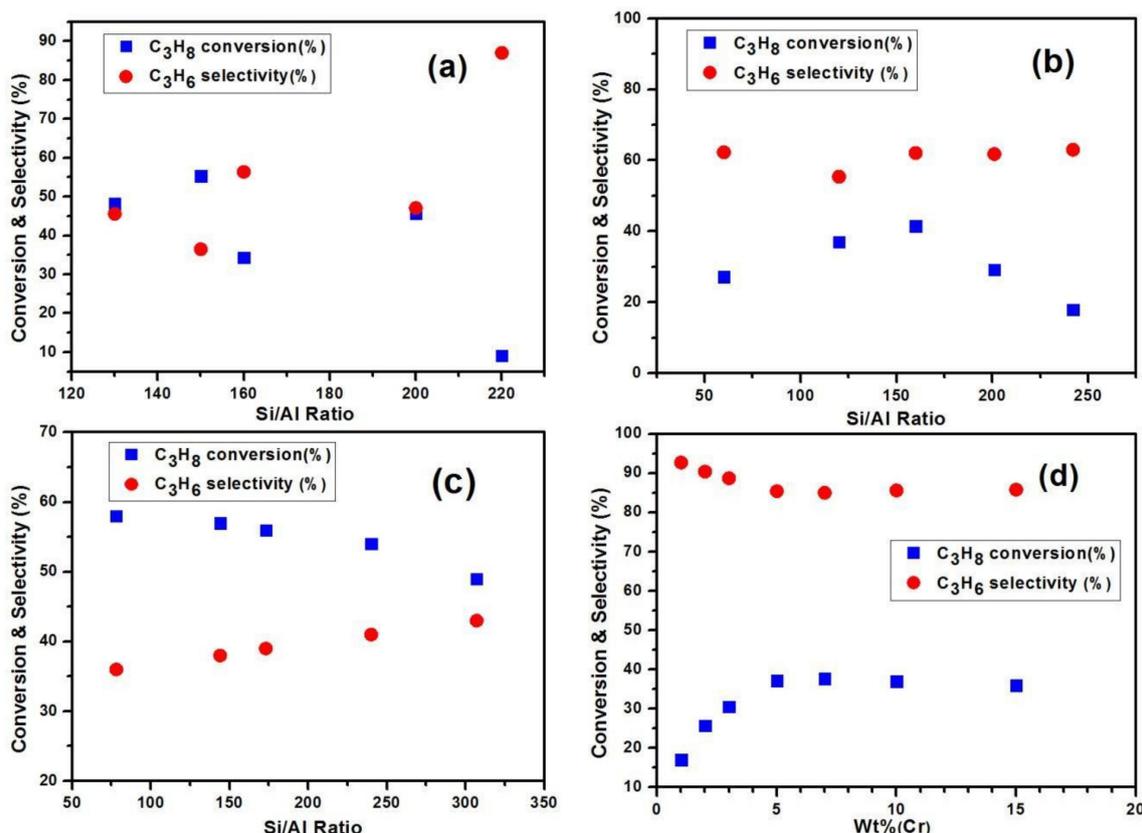


Figure 7. Influence of Si/Al proportion on the efficiency of (a) Ga₂O₃/ZSM-48 zeolites (Reproduced from [118]; copyright (2012), Elsevier), (b) ZnO-HZSM-5 zeolites in the oxidative dehydrogenation of propane along with CO₂ (Reproduced from [105]; copyright (2009), Elsevier), (c) Ga₂O₃/M-HZSM-5 zeolites in the absence of CO₂ (Reproduced from [118]; copyright (2012), Elsevier), (d) Influence of Cr substance on the effectiveness of Cr/SBA-15 in the carriage of CO₂ (Reproduced from [128]; copyright (2012), Elsevier).

4. Conclusions

This review article has comprised a number of CO₂ conversions, which are still in the research scale. These promising technologies are mitigating the continuously increasing atmospheric CO₂ concentration. Among the methods employing CO₂, the ethyl benzene ODH process has seen significant progress. Currently, most of the ethylbenzene dehydrogenation plants apply the oxidative dehydrogenation method, which leads to large heat losses upon compression at the gas–liquid separator. Further, this reaction is thermodynamically restrictive and energy intensive. Several industrial companies such as SABIC (Saudi Basic Industry Corporation, Saudi Arabia), Samsung General Co. in south Korea have tested the catalytic consummation for this method. The commercial implementation of such a process may support the economics of styrene monomer production. According to European Rubber Journal (ERJ), Asahi Kasei Chemical Company’s (Japan) 6th generation SBR (Styrene-butadiene rubber) is currently being tested by many customers in the world with positive feedback and company is planning to commercialize some grades in 2021. Moreover, Trinseo’s highly functionalized SPRINTAN™ 918S Solution-Styrene Butadiene Rubber (S-SBR) has awarded second position in the elastomers for sustainability initiative of the European Rubber Journal. Based on lab indicator data confirmed by tire customers, grade 918S (compared to non-functionalized high-grip SSBR) improves fuel efficiency of the whole car approximately 1.5%. Considering in Europe alone, the benefit of this increased fuel efficiency would translate in approximately 540 tons less fuel consumed or a reduction of CO₂ emissions by 1.3 million tons.

Several methods using CO₂ as a mild oxidant have appeared in the technology sector. It is a long-term goal and alluring dream for chemical engineers to establish commercial industries based on the utilization of CO₂. Challenges for the commercial utilization of this technology include the process rate required to ensure CO₂ conversion with low coke deposition, the need to decrease energy expenditure, and the need for improved catalysts offering higher conversion. Despite the challenges, there is great room for catalyst improvement in these sectors. Recently, the carbon XPRIZE is a \$20 million competition to capture and CO₂ conversion which is jointly funded by COSIA (Canada's Oil Sends Innovation Alliance) [129]. Most of the countries' governments are concern about climate changes with a high priority. China, the world's largest energy consumer and carbon emitter, announced USD 360 billion in renewable energy investments by 2020 to reduce carbon emissions [130]. Canada has implemented federally a carbon pricing policy with a current tax of USD 10/ton CO₂ and a steady rise to USD 50/ton CO₂ nationwide by 2022. However, the positive effects of CO₂ in benzene hydroxylation over commercial and hierarchical zeolites in the liquid phase as well as the gas phase are under investigation by our group, wherein the byproducts are various aromatic compounds. The recycling of CO₂ from the atmosphere to fuels, chemicals will lead to a real sustainable future for humanity. We expect that the use of CO₂ as a promoter and as a mild oxidant at the laboratory level can be translated to the industrial scale in the future, thus contributing also to the world economy.

Author Contributions: S.T.R.: Writing original draft; J.-R.C.: Editing; J.-H.L.: Editing; S.-J.P.: Writing review & editing. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Technology Innovation Program (or Industrial Strategic Technology Development Program-Development of technology on materials and components) (20010881, Development of ACF for rigid (COG)/ flexible (COP) and secured mass production by developing core material technology for localizing latent hardener for low temperature fast curing) funded By the Ministry of Trade, Industry & Energy (MOTIE, Korea) and supported by Korea Evaluation institute of Industrial Technology (KEIT) through the Carbon Cluster Construction project [10083586, Development of petroleum based graphite fibers with ultra-high thermal conductivity] funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea).

Conflicts of Interest: The authors declare that they have no conflicts of interest.

References

1. Kar, S.; Goeppert, A.; Prakash, G.K.S. Integrated CO₂ Capture and Conversion to Formate and Methanol: Connecting Two Threads. *Acc. Chem. Res.* **2019**, *52*, 2892–2903. [[CrossRef](#)] [[PubMed](#)]
2. Smol, J.P. Climate Change: A Planet in flux. *Nature* **2012**, *483*, 12–15. [[CrossRef](#)] [[PubMed](#)]
3. Ross, M.B.; De Luna, P.; Li, Y.; Dinh, C.-T.; Kim, D.; Yang, P.; Sargent, E.H. Designing materials for electrochemical carbon dioxide recycling. *Nat. Catal.* **2019**, *2*, 648–658. [[CrossRef](#)]
4. De Luna, P.; Hahnert, C.; Higgins, D.; Jaffer, S.A.; Jaramillo, T.F.; Sargent, E.H. What would it take for renewably powered electrosynthesis to displace petrochemical processes? *Science* **2019**, *364*. [[CrossRef](#)]
5. Nugent, P.; Belmabkhout, Y.; Burd, S.D.; Cairns, A.J.; Luebke, R.; Forrest, K.; Pham, T.; Ma, S.; Space, B.; Wojtas, L.; et al. Porous materials with optimal adsorption thermodynamics and kinetics for CO₂ separation. *Nature* **2013**, *495*, 80–84. [[CrossRef](#)]
6. Rehman, A.; Park, S.-J. From chitosan to urea-modified carbons: Tailoring the ultra-microporosity for enhanced CO₂ adsorption. *Carbon* **2020**, *159*, 625–637. [[CrossRef](#)]
7. Lee, S.H.; Sullivan, I.; Larson, D.M.; Liu, G.; Toma, F.M.; Xiang, C.; Drisdell, W.S. Correlating Oxidation State and Surface Area to Activity from Operando Studies of Copper CO Electroreduction Catalysts in a Gas Fed Device. *ACS Catal.* **2020**, *10*, 8000–8011. [[CrossRef](#)]
8. Han, L.; Zhou, W.; Xiang, C. High-Rate Electrochemical Reduction of Carbon Monoxide to Ethylene Using Cu-Nanoparticles Based Gas Diffusion Electrodes. *ACS Energy Lett.* **2018**, *3*, 855–860. [[CrossRef](#)]
9. Heo, Y.J.; Park, S.-J. Facile Synthesis of MgO-Modified Carbon Adsorbents with Microwave-Assisted Methods: Effect of MgO Particles and Porosities on CO₂ Capture. *Sci. Rep.* **2017**, *7*, 1–9. [[CrossRef](#)] [[PubMed](#)]
10. Qi, S.-C.; Wu, J.-K.; Lu, J.; Yu, G.-X.; Zhu, R.R.; Liu, Y.; Liu, X.-Q.; Sun, L.-B. Underlying mechanism of CO₂ adsorption onto conjugated azacyclo-copolymers: N-doped adsorbents capture CO₂ chiefly through acid-base interaction? *J. Mater. Chem. A* **2019**, *7*, 17842–17853. [[CrossRef](#)]

11. Qi, S.C.; Liu, Y.; Peng, A.Z.; Xue, D.M.; Liu, X.; Liu, X.Q.; Sun, L.B. Fabrication of porous carbons from mesitylene for highly efficient CO₂ capture: A rational choice improving the carbon loop. *Chem. Eng. J.* **2019**, *361*, 945–952. [[CrossRef](#)]
12. Rehman, A.; Park, S.-J. Tunable nitrogen-doped microporous carbons: Delineating the role of optimum pore size for enhanced CO₂ adsorption. *Chem. Eng. J.* **2019**, *362*, 731–742. [[CrossRef](#)]
13. Jessop, P.G.; Ikariya, T.; Noyori, R. Homogeneous catalysis in supercritical fluids. *Science* **1995**, *269*, 1065–1069. [[CrossRef](#)]
14. Musie, G.; Wei, M.; Subramaniam, B.; Busch, D.H. Catalytic oxidations in carbon dioxide-based reaction media, including novel CO₂-expanded phases. *Coord. Chem. Rev.* **2001**, *219–221*, 789–820. [[CrossRef](#)]
15. Heldebrant, D.J.; Jessop, P.G.; Thomas, C.A.; Eckert, C.A.; Liotta, C.L. The reaction of 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) with carbon dioxide. *J. Org. Chem.* **2005**, *70*, 5335–5338. [[CrossRef](#)]
16. Chang, J.S.; Vislovskiy, V.P.; Park, M.S.; Hong, D.Y.; Yoo, J.S.; Park, S.E. Utilization of carbon dioxide as soft oxidant in the dehydrogenation of ethyl benzene over supported vanadium-antimony oxide catalysts. *Green Chem.* **2003**, *5*, 587–590. [[CrossRef](#)]
17. Park, M.S.; Chang, J.S.; Kim, D.S.; Park, S.-E. Oxidative dehydrogenation of ethyl benzene with carbon dioxide over zeolite-supported iron oxide catalysts. *Res. Chem. Intermed.* **2002**, *28*, 461–469. [[CrossRef](#)]
18. Sakakura, T.; Choi, J.C.; Yasuda, H. Transformation of carbon dioxide. *Chem. Rev.* **2007**, *107*, 2365–2387. [[CrossRef](#)]
19. Reddy, B.M.; Lakshmanan, P.; Loidant, S.; Yamada, Y.; Kobayashi, T.; López-Cartes, C.; Rojas, T.C.; Fernández, A. Structural characterization and oxidative dehydrogenation Activity of $v2O_5/CexZr1-xO_2/SiO_2$ catalysts. *J. Phys. Chem. B* **2006**, *110*, 9140–9147. [[CrossRef](#)]
20. Yoo, J.S.; Lin, P.S.; Elfline, S.D. Gas-phase oxygen oxidations of alkyl aromatics over CVD Fe/Mo/borosilicate molecular sieve. II. The role of carbon dioxide as a co-oxidant. *Appl. Catal. A Gen.* **1993**, *106*, 259–273. [[CrossRef](#)]
21. Sun, A.; Qin, Z.; Wang, J. Reaction coupling of ethylbenzene dehydrogenation with water-gas shift. *Appl. Catal. A Gen.* **2002**, *234*, 179–189. [[CrossRef](#)]
22. Ansari, M.B.; Park, S.E. Carbon dioxide utilization as a soft oxidant and promoter in catalysis. *Energy Environ. Sci.* **2012**, *5*, 9419–9437. [[CrossRef](#)]
23. Abanades, S.; Le Gal, A. CO₂ splitting by thermo-chemical looping based on ZrxCe1-xO₂ oxygen carriers for synthetic fuel generation. *Fuel* **2012**, *102*, 180–186. [[CrossRef](#)]
24. Wang, S.; Wang, X. Imidazolium ionic liquids, imidazolylidene heterocyclic carbenes, and zeolitic imidazolate frameworks for CO₂ capture and photochemical reduction. *Angew. Chemie Int. Ed.* **2016**, *55*, 2308–2320. [[CrossRef](#)] [[PubMed](#)]
25. Nikulshina, V.; Hirsch, D.; Mazzotti, M.; Steinfeld, A. CO₂ capture from air and co-production of H₂ via the Ca(OH)₂-CaCO₃ cycle using concentrated solar power-Thermodynamic analysis. *Energy* **2006**, *31*, 1715–1725. [[CrossRef](#)]
26. Spinner, N.S.; Vega, J.A.; Mustain, W.E. Recent progress in the electrochemical conversion and utilization of CO₂. *Catal. Sci. Technol.* **2012**, *2*, 19–28. [[CrossRef](#)]
27. Singh, G.; Lakhi, K.S.; Ramadass, K.; Sathish, C.I.; Vinu, A. High-Performance Biomass-Derived Activated Porous Biocarbons for Combined Pre- and Post-Combustion CO₂ Capture. *ACS Sustain. Chem. Eng.* **2019**, *7*, 7412–7420. [[CrossRef](#)]
28. Grice, K.A. Carbon dioxide reduction with homogenous early transition metal complexes: Opportunities and challenges for developing CO₂ catalysis. *Coord. Chem. Rev.* **2017**, *336*, 78–95. [[CrossRef](#)]
29. Bartholomew, C.H. *Catalyst Deactivation 1991*; Elsevier: Amsterdam, The Netherlands, 1991; pp. 96–112.
30. Denekamp, I.M.; Antens, M.; Slot, T.K.; Rothenberg, G. Selective Catalytic Oxidation of Cyclohexene with Molecular Oxygen: Radical Versus Nonradical Pathways. *ChemCatChem* **2018**, *10*, 1035–1041. [[CrossRef](#)]
31. Ansari, M.B.; Min, B.H.; Mo, Y.H.; Park, S.-E. CO₂ activation and promotional effect in the oxidation of cyclic olefins over mesoporous carbon nitrides. *Green Chem.* **2011**, *13*, 1416–1421. [[CrossRef](#)]
32. Aresta, M.; Tommasi, I.; Quaranta, E.; Fragale, C.; Tranquille, M.; Galan, F.; Fouassier, M. Mechanism of formation of peroxycarbonates RhOOC(O)O(Cl)(P)₃ and Their Reactivity as Oxygen Transfer Agents Mimicking Monooxygenases. The First Evidence of CO₂ Insertion into the O-O Bond of Rh(η^2 -O₂) Complexes. *Inorg. Chem.* **1996**, *35*, 4254–4260. [[CrossRef](#)] [[PubMed](#)]

33. Iwata, R.; Ido, T.; Fujisawa, Y.; Yamazaki, S. On-line interconversion of [¹⁵O]O₂ and [¹⁵O]CO₂ via metal oxide by isotopic exchange. *Int. J. Radiat. Appl. Instrum. Part A*. **1988**, *39*, 1207–1211. [[CrossRef](#)]
34. Nair, V.; Varghese, V.; Paul, R.R.; Jose, A.; Sinu, C.R.; Menon, R.S. NHC catalyzed transformation of aromatic aldehydes to acids by carbon dioxide: An unexpected reaction. *Org. Lett.* **2010**, *12*, 2653–2655. [[CrossRef](#)]
35. Chiang, P.C.; Bode, J.W. On the role of CO₂ in NHC-catalyzed oxidation of aldehydes. *Org. Lett.* **2011**, *13*, 2422–2425. [[CrossRef](#)] [[PubMed](#)]
36. Gu, L.; Zhang, Y. Unexpected CO₂ splitting reactions to form CO with N-heterocyclic carbenes as organocatalysts and aromatic aldehydes as oxygen acceptors. *J. Am. Chem. Soc.* **2010**, *132*, 914–915. [[CrossRef](#)]
37. Lane, B.S.; Vogt, M.; De Rose, V.J.; Kevin, B. Manganese-Catalyzed Epoxidations of Alkenes in Bicarbonate Solutions. *J. Am. Chem. Soc.* **2002**, *124*, 11946–11954. [[CrossRef](#)]
38. Park, S.-E.; Yoo, J.S. *Studies in Surface Science and Catalysis 153*; Elsevier: Amsterdam, The Netherlands, 2004; pp. 303–314.
39. Cavani, F.; Trifiro, F. Alternative Processes for the Production of Sponge Iron. *Appl. Catal. A Gen.* **1995**, *133*, 219–239. [[CrossRef](#)]
40. Li, X.; Li, W. Effect of TiO₂ loading on the activity of V/TiO₂-Al₂O₃ in the catalytic oxidehydrogenation of ethylbenzene with carbon dioxide. *Front. Chem. Eng. China* **2010**, *4*, 142–146. [[CrossRef](#)]
41. Nowicka, E.; Reece, C.; Althahban, S.M.; Mohammed, K.M.H.; Kondrat, S.A.; Morgan, D.J.; He, Q.; Willock, D.J.; Golunski, S.; Kiely, C.J.; et al. Elucidating the Role of CO₂ in the Soft Oxidative Dehydrogenation of Propane over Ceria-Based Catalysts. *ACS Catal.* **2018**, *8*, 3454–3468. [[CrossRef](#)]
42. Kovacevic, M.; Agarwal, S.; Mojet, B.L.; Van Ommen, J.G.; Lefferts, L. The effects of morphology of cerium oxide catalysts for dehydrogenation of ethylbenzene to styrene. *Appl. Catal. A Gen.* **2015**, *505*, 354–364. [[CrossRef](#)]
43. Rao, R.; Zhang, Q.; Liu, H.; Yang, H.; Ling, Q.; Yang, M.; Zhang, A.; Chen, W. Enhanced catalytic performance of CeO₂ confined inside carbon nanotubes for dehydrogenation of ethylbenzene in the presence of CO₂. *J. Mol. Catal. A Chem.* **2012**, *363–364*, 283–290. [[CrossRef](#)]
44. Rao, R.; Yang, M.; Ling, Q.; Li, C.; Zhang, Q.; Yang, H.; Zhang, A. A novel route of enhancing oxidative catalytic activity: Hydroxylation of MWCNTs induced by sectional defects. *Catal. Sci. Technol.* **2014**, *4*, 665–671. [[CrossRef](#)]
45. Sakurai, Y.; Suzuki, T.; Ikenaga, N.O.; Suzuki, T. Dehydrogenation of ethylbenzene with an activated carbon-supported vanadium catalyst. *Appl. Catal. A Gen.* **2000**, *192*, 281–288. [[CrossRef](#)]
46. Fan, H.; Feng, J.; Li, X.; Guo, Y.; Li, W.; Xie, K. Ethylbenzene dehydrogenation to styrene with CO₂ over V₂O₅(001): A periodic density functional theory study. *Chem. Eng. Sci.* **2015**, *135*, 403–411. [[CrossRef](#)]
47. Rao, K.N.; Reddy, B.M.; Abhishek, B.; Seo, Y.H.; Jiang, N.; Park, S.E. Effect of ceria on the structure and catalytic activity of V₂O₅/TiO₂-ZrO₂ for oxidehydrogenation of ethylbenzene to styrene utilizing CO₂ as soft oxidant. *Appl. Catal. B Environ.* **2009**, *91*, 649–656. [[CrossRef](#)]
48. Liu, Z.W.; Wang, C.; Fan, W.B.; Liu, Z.T.; Hao, Q.Q.; Long, X.; Lu, J.; Wang, J.G.; Qin, Z.F.; Su, D.S. V₂O₅/Ce_{0.6}Zr_{0.4}O₂-Al₂O₃ as an efficient catalyst for the oxidative dehydrogenation of ethylbenzene with carbon dioxide. *ChemSusChem* **2011**, *4*, 341–345. [[CrossRef](#)]
49. Burri, A.; Jiang, N.; Ji, M.; Park, S.-E.; Khalid, Y. Oxidative dehydrogenation of ethylbenzene to styrene with CO₂ over V₂O₅-Sb₂O₅-CeO₂/TiO₂-ZrO₂ catalysts. *Top. Catal.* **2013**, *56*, 1724–1730. [[CrossRef](#)]
50. Liu, B.S.; Rui, G.; Chang, R.Z.; Au, C.T. Dehydrogenation of ethylbenzene to styrene over LaVO_x/SBA-15 catalysts in the presence of carbon dioxide. *Appl. Catal. A Gen.* **2008**, *335*, 88–94. [[CrossRef](#)]
51. Li, Z.; Su, K.; Cheng, B.; Shen, D.; Zhou, Y. Effects of VO_x/AlMCM-41 surface structure on ethyl benzene oxidehydrogenation in the presence of CO₂. *Catal. Lett.* **2010**, *135*, 135–140. [[CrossRef](#)]
52. Jiang, N.; Burri, A.; Park, S.-E. Ethylbenzene to styrene over ZrO₂-based mixed metal oxide catalysts with CO₂ as soft oxidant. *Chin. J. Catal.* **2016**, *37*, 3–15. [[CrossRef](#)]
53. Reddy, B.M.; Khan, A. Recent advances on TiO₂-ZrO₂ mixed oxides as catalysts and catalyst supports. *Catal. Rev. Sci. Eng.* **2005**, *47*, 257–296. [[CrossRef](#)]
54. Jiang, N.; Han, D.S.; Park, S.-E. Direct synthesis of mesoporous silicalite-1 supported TiO₂-ZrO₂ for the dehydrogenation of EB to styrene with CO₂. *Catal. Today* **2009**, *141*, 344–348. [[CrossRef](#)]
55. Manríquez, M.E.; López, T.; Gómez, R.; Navarrete, J. Preparation of TiO₂-ZrO₂ mixed oxides with controlled acid-basic properties. *J. Mol. Catal. A Chem.* **2004**, *220*, 229–237. [[CrossRef](#)]

56. Zangeneh, F.T.; Sahebdehfar, S.; Ravanchi, M.T. Conversion of carbon dioxide to valuable petrochemicals: An approach to clean development mechanism. *J. Nat. Gas Chem.* **2011**, *20*, 219–231. [[CrossRef](#)]
57. Balasamy, R.J.; Tope, B.B.; Khurshid, A.; Al-Ali, A.A.S.; Atanda, L.A.; Sagata, K.; Asamoto, M.; Yahiro, H.; Nomura, K.; Sano, T.; et al. Ethylbenzene dehydrogenation over FeOx/(Mg,Zn)(Al)O catalysts derived from hydrotalcites: Role of MgO as basic sites. *Appl. Catal. A Gen.* **2011**, *398*, 113–122. [[CrossRef](#)]
58. Braga, T.P.; Pinheiro, A.N.; Teixeira, C.V.; Valentini, A. Dehydrogenation of ethylbenzene in the presence of CO₂ using a catalyst synthesized by polymeric precursor method. *Appl. Catal. A Gen.* **2009**, *366*, 193–200. [[CrossRef](#)]
59. Pochamoni, R.; Narani, A.; Varkolu, M.; Dhar Gudimella, M.; Prasad Potharaju, S.S.; Burri, D.R.; Rao Kamaraju, S.R. Studies on ethylbenzene dehydrogenation with CO₂ as soft oxidant over Co₃O₄/COK-12 catalysts. *J. Chem. Sci.* **2015**, *127*, 701–709. [[CrossRef](#)]
60. Zhao, G.; Chen, H.; Li, J.; Wang, Q.; Wang, Y.; Ma, S.; Zhu, Z. Acid-based co-catalysis for oxidative dehydrogenation of ethylbenzene to styrene with CO₂ over X zeolite modified by alkali metal cation exchange. *RSC Adv.* **2015**, *5*, 75787–75793. [[CrossRef](#)]
61. Periyasamy, K.; Aswathy, V.T.; Ashok Kumar, V.; Manikandan, M.; Shukla, R.; Tyagi, A.K.; Raja, T. An efficient robust fluorite CeZrO_{4-δ} oxide catalyst for the eco-benign synthesis of styrene. *RSC Adv.* **2015**, *5*, 3619–3626. [[CrossRef](#)]
62. Mukherjee, D.; Park, S.-E.; Reddy, B.M. CO₂ as a soft oxidant for oxidative dehydrogenation reaction: An eco benign process for industry. *J. CO₂ Util.* **2016**, *16*, 301–312. [[CrossRef](#)]
63. Sato, S.; Ohhara, M.; Sodesawa, T.; Nozaki, F. Combination of ethylbenzene dehydrogenation and carbon dioxide shift-reaction over a sodium oxide/alumina catalyst. *Appl. Catal.* **1988**, *37*, 207–215. [[CrossRef](#)]
64. Chen, S.; Qin, Z.; Wang, G.; Dong, M.; Wang, J. Promoting effect of carbon dioxide on the dehydrogenation of ethylbenzene over silica-supported vanadium catalysts. *Fuel* **2013**, *109*, 43–48. [[CrossRef](#)]
65. Burri, D.R.; Choi, K.M.; Han, S.C.; Burri, A.; Park, S.-E. Dehydrogenation of ethylbenzene to styrene with CO₂ over TiO₂-ZrO₂ bifunctional catalyst. *Bull. Korean Chem. Soc.* **2007**, *28*, 53–58.
66. Burri, D.R.; Choi, K.M.; Han, S.C.; Burri, A.; Park, S.-E. Selective conversion of ethylbenzene into styrene over K₂O/TiO₂-ZrO₂ catalysts: Unified effects of K₂O and CO₂. *J. Mol. Catal. A Chem.* **2007**, *269*, 58–63. [[CrossRef](#)]
67. Burri, A.; Jiang, N.; Park, S.-E. High surface area TiO₂-ZrO₂ prepared by caustic solution treatment, and its catalytic efficiency in the oxidehydrogenation of para-ethyl toluene by CO₂. *Catal. Sci. Technol.* **2012**, *2*, 514–520. [[CrossRef](#)]
68. Burri, D.R.; Choi, K.M.; Han, D.S.; Sujandi; Jiang, N.; Burri, A.; Park, S.-E. Oxidative dehydrogenation of ethylbenzene to styrene with CO₂ over SnO₂-ZrO₂ mixed oxide nanocomposite catalysts. *Catal. Today* **2008**, *131*, 173–178. [[CrossRef](#)]
69. Burri, D.R.; Choi, K.M.; Han, D.S.; Koo, J.B.; Park, S.-E. CO₂ utilization as an oxidant in the dehydrogenation of ethylbenzene to styrene over MnO₂-ZrO₂ catalysts. *Catal. Today* **2006**, *115*, 242–247. [[CrossRef](#)]
70. Rahmani, F.; Haghghi, M.; Amini, M. The beneficial utilization of natural zeolite in preparation of Cr/clinoptilolite nanocatalyst used in CO₂-oxidative dehydrogenation of ethane to ethylene. *J. Ind. Eng. Chem.* **2015**, *31*, 142–155. [[CrossRef](#)]
71. Mimura, N.; Takahara, I.; Inaba, M.; Okamoto, M.; Murata, K. High-performance Cr/H-ZSM-5 catalysts for oxidative dehydrogenation of ethane to ethylene with CO₂ as an oxidant. *Catal. Commun.* **2002**, *3*, 257–262. [[CrossRef](#)]
72. Liu, L.; Li, H.; Zhang, Y. A comparative study on catalytic performances of chromium incorporated and supported mesoporous MSU-x catalysts for the oxidehydrogenation of ethane to ethylene with carbon dioxide. *Catal. Today* **2006**, *115*, 235–241. [[CrossRef](#)]
73. Shi, X.; Ji, S.; Wang, K. Oxidative dehydrogenation of ethane to ethylene with carbon dioxide over Cr-Ce/SBA-15 catalysts. *Catal. Lett.* **2008**, *125*, 331–339. [[CrossRef](#)]
74. Deng, S.; Li, S.; Li, H.; Zhang, Y. Oxidative dehydrogenation of ethane to ethylene with CO₂ over Fe-Cr/ZrO₂ catalysts. *Ind. Eng. Chem. Res.* **2009**, *48*, 7561–7566. [[CrossRef](#)]
75. Shi, X.; Ji, S.; Li, C. Oxidative dehydrogenation of ethane with CO₂ over novel Cr/SBA-15/Al₂O₃/FeCrAl monolithic catalysts. *Energy Fuels* **2008**, *22*, 3631–3638. [[CrossRef](#)]
76. Tedeeva, M.A.; Kustov, A.L.; Pribytkov, P.V.; Leonov, A.V.; Dunaev, S.F. Dehydrogenation of Propane with CO₂ on Supported CrOx/SiO₂ Catalysts. *Russ. J. Phys. Chem. A* **2018**, *92*, 2403–2407. [[CrossRef](#)]

77. Wang, S.; Murata, K.; Hayakawa, T.; Hamakawa, S.; Suzuki, K. Dehydrogenation of ethane with carbon dioxide over supported chromium oxide catalysts. *Appl. Catal. A Gen.* **2000**, *196*, 1–8. [[CrossRef](#)]
78. Weckhuysen, B.M.; Schoonheydt, R.A.; Jehng, J.M.; Wachs, I.E.; Cho, S.J.; Ryoo, R.; Kijlstra, S.; Poels, E. Combined DRS-RS-EXAFS-XANES-TPR study of supported chromium catalysts. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 3245–3253. [[CrossRef](#)]
79. Mimura, N.; Okamoto, M.; Yamashita, H.; Oyama, S.T.; Murata, K. Oxidative dehydrogenation of ethane over Cr/ZSM-5 catalysts using CO₂ as an oxidant. *J. Phys. Chem. B* **2006**, *110*, 21764–21770. [[CrossRef](#)]
80. Heracleous, E.; Lemonidou, A.A. Ni-Nb-O mixed oxides as highly active and selective catalysts for ethene production via ethane oxidative dehydrogenation. Part I: Characterization and catalytic performance. *J. Catal.* **2006**, *237*, 162–174. [[CrossRef](#)]
81. Heracleous, E.; Lemonidou, A.A. Ni-Nb-O mixed oxides as highly active and selective catalysts for ethene production via ethane oxidative dehydrogenation. Part II: Mechanistic aspects and kinetic modeling. *J. Catal.* **2006**, *237*, 175–189.
82. Heracleous, E.; Delimitis, A.; Nalbandian, L.; Lemonidou, A.A. HRTEM characterization of the nanostructural features formed in highly active Ni-Nb-O catalysts for ethane ODH. *Appl. Catal. A Gen.* **2007**, *325*, 220–226. [[CrossRef](#)]
83. Koirala, R.; Buechel, R.; Krumeich, F.; Pratsinis, S.E.; Baiker, A. Oxidative dehydrogenation of ethane with CO₂ over flame-made Ga-loaded TiO₂. *ACS Catal.* **2015**, *5*, 690–702. [[CrossRef](#)]
84. Cheng, Y.; Zhang, F.; Zhang, Y.; Miao, C.; Hua, W.; Yue, Y.; Gao, Z. Oxidative dehydrogenation of ethane with CO₂ over Cr supported on submicron ZSM-5 zeolite. *Chinese J. Catal.* **2015**, *36*, 1242–1248. [[CrossRef](#)]
85. Ramesh, Y.; Thirumala Bai, P.; Hari Babu, B.; Lingaiah, N.; Rama Rao, K.S.; Prasad, P.S.S. Oxidative dehydrogenation of ethane to ethylene on Cr₂O₃/Al₂O₃-ZrO₂ catalysts: The influence of oxidizing agent on ethylene selectivity. *Appl. Petrochem. Res.* **2014**, *4*, 247–252. [[CrossRef](#)]
86. Deng, S.; Li, H.; Li, S.; Zhang, Y. Activity and characterization of modified Cr₂O₃/ZrO₂ nano-composite catalysts for oxidative dehydrogenation of ethane to ethylene with CO₂. *J. Mol. Catal. A Chem.* **2007**, *268*, 169–175. [[CrossRef](#)]
87. Yashima, T.; Sato, K.; Hayasaka, T.; Hara, N. Alkylation on synthetic zeolites. III. Alkylation of toluene with methanol and formaldehyde on alkali cation exchanged zeolites. *J. Catal.* **1972**, *26*, 303–312. [[CrossRef](#)]
88. Rossetti, I.; Bencini, E.; Trentini, L.; Forni, L. Study of the deactivation of a commercial catalyst for ethylbenzene dehydrogenation to styrene. *Appl. Catal. A Gen.* **2005**, *292*, 118–123. [[CrossRef](#)]
89. Meima, G.R.; Menon, P.G. Catalyst deactivation phenomena in styrene production. *Appl. Catal. A Gen.* **2001**, *212*, 239–245. [[CrossRef](#)]
90. Sindorenko, L.N.; Galich, P.N.; Gutirya, V.S. Condensation of toluene and methanol upon synthetic zeolites containing ion-exchange cations of alkali metals. *Dokl. Akad. Nauk. SSSR* **1967**, *173*, 132–133.
91. Seo, D.W.; Rahman, S.T.; Reddy, B.M.; Park, S.-E. Carbon dioxide assisted toluene side-chain alkylation with methanol over Cs-X zeolite catalyst. *J. CO₂ Util.* **2018**, *26*, 254–261. [[CrossRef](#)]
92. Hattori, H. Solid base catalysts: Fundamentals and their applications in organic reactions. *Appl. Catal. A Gen.* **2015**, *504*, 103–109. [[CrossRef](#)]
93. Yoo, K.S.; Smirniotis, P.G. Zeolites-catalyzed alkylation of isobutane with 2-butene: Influence of acidic properties. *Catal. Lett.* **2005**, *103*, 249–255. [[CrossRef](#)]
94. Alabi, W.O.; Tope, B.B.; Jermy, R.B.; Aitani, A.M.; Hattori, H.; Al-Khattaf, S.S. Modification of Cs-X for styrene production by side-chain alkylation of toluene with methanol. *Catal. Today* **2014**, *226*, 117–123. [[CrossRef](#)]
95. Yoo, K.; Smirniotis, P.G. The deactivation pathway of one-dimensional zeolites, LTL and ZSM-12, for alkylation of isobutane with 2-butene. *Appl. Catal. A Gen.* **2003**, *246*, 243–251. [[CrossRef](#)]
96. Yoo, K.; Burckle, E.C.; Smirniotis, P.G. Isobutane/2-butene alkylation using large-pore zeolites: Influence of pore structure on activity and selectivity. *J. Catal.* **2002**, *211*, 6–18. [[CrossRef](#)]
97. Han, H.; Liu, M.; Nie, X.; Ding, F.; Wang, Y.; Li, J.; Guo, X.; Song, C. The promoting effects of alkali metal oxide in side-chain alkylation of toluene with methanol over basic zeolite X. *Microporous Mesoporous Mater.* **2016**, *234*, 61–72. [[CrossRef](#)]
98. Itoh, H.; Hattori, T.; Suzuki, K.; Murakami, Y. Role of acid and base sites in the side-chain alkylation of alkylbenzenes with methanol on two-ion-exchanged zeolites. *J. Catal.* **1983**, *79*, 21–33. [[CrossRef](#)]

99. Tope, B.B.; Alabi, W.O.; Aitani, A.M.; Hattori, H.; Al-Khattaf, S.S. Side-chain alkylation of toluene with methanol to styrene over cesium ion-exchanged zeolite X modified with metal borates. *Appl. Catal. A Gen.* **2012**, *443–444*, 214–220. [[CrossRef](#)]
100. Philippou, A.; Anderson, M.W. Solid-State NMR Investigation of the Alkylation of Toluene with Methanol over Basic Zeolite X. *J. Am. Chem. Soc.* **1994**, *116*, 5774–5783. [[CrossRef](#)]
101. Jiang, N.; Jin, H.; Jeong, E.-Y.; Park, S.-E. Mgo Encapsulated Mesoporous Zeolite for the Side Chain Alkylation of Toluene with Methanol. *J. Nanosci. Nanotechnol.* **2010**, *10*, 227–232. [[CrossRef](#)]
102. Hattori, H.; Alabi, W.O.; Jermy, B.R.; Aitani, A.M.; Al-Khattaf, S.S. Pathway to ethylbenzene formation in side-chain alkylation of toluene with methanol over cesium ion-exchanged zeolite X. *Catal. Lett.* **2013**, *143*, 1025–1029. [[CrossRef](#)]
103. Mikkelsen, M.; Jørgensen, M.; Krebs, F.C. The teraton challenge. A review of fixation and transformation of carbon dioxide. *Energy Environ. Sci.* **2010**, *3*, 43–81. [[CrossRef](#)]
104. Cavani, F.; Ballarini, N.; Cericola, A. Oxidative dehydrogenation of ethane and propane: How far from commercial implementation? *Catal. Today* **2007**, *127*, 113–131. [[CrossRef](#)]
105. Ren, Y.; Zhang, F.; Hua, W.; Yue, Y.; Gao, Z. ZnO supported on high silica HZSM-5 as new catalysts for dehydrogenation of propane to propene in the presence of CO₂. *Catal. Today* **2009**, *148*, 316–322. [[CrossRef](#)]
106. Chen, M.; Xu, J.; Liu, Y.M.; Cao, Y.; He, H.Y.; Zhuang, J.H. Supported indium oxide as novel efficient catalysts for dehydrogenation of propane with carbon dioxide. *Appl. Catal. A Gen.* **2010**, *377*, 35–41. [[CrossRef](#)]
107. Schimmoeller, B.; Jiang, Y.; Pratsinis, S.E.; Baiker, A. Structure of flame-made vanadia/silica and catalytic behavior in the oxidative dehydrogenation of propane. *J. Catal.* **2010**, *274*, 64–75. [[CrossRef](#)]
108. Liu, Y.M.; Cao, Y.; Yan, S.R.; Dai, W.L.; Fan, K.N. Highly effective oxidative dehydrogenation of propane over vanadia supported on mesoporous SBA-15 silica. *Catal. Lett.* **2003**, *88*, 61–67. [[CrossRef](#)]
109. Santamaría-González, J.; Mérida-Robles, J.; Alcántara-Rodríguez, M.; Maireles-Torres, P.; Rodríguez-Castellón, E.; Jiménez-López, A. Catalytic behaviour of chromium supported mesoporous MCM-41 silica in the oxidative dehydrogenation of propane. *Catal. Lett.* **2000**, *64*, 209–214. [[CrossRef](#)]
110. Davies, T.; Taylor, S.H. The oxidative dehydrogenation of propane using gallium-molybdenum oxide-based catalysts. *J. Mol. Catal. A Chem.* **2004**, *220*, 77–84. [[CrossRef](#)]
111. Raju, G.; Reddy, B.M.; Abhishek, B.; Mo, Y.H.; Park, S.-E. Synthesis of C₄ olefins from n-butane over a novel VOx/SnO₂-ZrO₂ catalyst using CO₂ as soft oxidant. *Appl. Catal. A Gen.* **2012**, *423–424*, 168–175. [[CrossRef](#)]
112. Atanga, M.A.; Rezaei, F.; Jawad, A.; Fitch, M.; Rownaghi, A.A. Oxidative dehydrogenation of propane to propylene with carbon dioxide. *Appl. Catal. B Environ.* **2018**, *220*, 429–445. [[CrossRef](#)]
113. Reddy, B.M.; Lee, S.C.; Han, D.S.; Park, S.-E. Utilization of carbon dioxide as soft oxidant for oxydehydrogenation of ethylbenzene to styrene over V₂O₅-CeO₂/TiO₂-ZrO₂ catalyst. *Appl. Catal. B Environ.* **2009**, *87*, 230–238. [[CrossRef](#)]
114. Uy, D.; O'Neill, A.E.; Xu, L.; Weber, W.H.; McCabe, R.W. Observation of cerium phosphate in aged automotive catalysts using Raman spectroscopy. *Appl. Catal. B Environ.* **2003**, *41*, 269–278. [[CrossRef](#)]
115. Armaroli, T.; Simon, L.J.; Digne, M.; Montanari, T.; Bevilacqua, M.; Valtchev, V.; Patarin, J.; Busca, G. Effects of crystal size and Si/Al ratio on the surface properties of H-ZSM-5 zeolites. *Appl. Catal. A Gen.* **2006**, *306*, 78–84. [[CrossRef](#)]
116. Thakkar, H.; Eastman, S.; Hajari, A.; Rownaghi, A.A.; Knox, J.C.; Rezaei, F. 3D-Printed Zeolite Monoliths for CO₂ Removal from Enclosed Environments. *ACS Appl. Mater. Interfaces* **2016**, *8*, 27753–27761. [[CrossRef](#)]
117. Thakkar, H.; Eastman, S.; Al-Mamoori, A.; Hajari, A.; Rownaghi, A.A.; Rezaei, F. Formulation of Aminosilica Adsorbents into 3D-Printed Monoliths and Evaluation of Their CO₂ Capture Performance. *ACS Appl. Mater. Interfaces* **2017**, *9*, 7489–7498. [[CrossRef](#)]
118. Ren, Y.; Wang, J.; Hua, W.; Yue, Y.; Gao, Z. Ga₂O₃/HZSM-48 for dehydrogenation of propane: Effect of acidity and pore geometry of support. *J. Ind. Eng. Chem.* **2012**, *18*, 731–736. [[CrossRef](#)]
119. Abello, M.C.; Gomez, M.F.; Ferretti, O. Oxidative conversion of propane over Al₂O₃-supported molybdenum and chromium oxides. *Catal. Lett.* **2003**, *87*, 43–49. [[CrossRef](#)]
120. Cherian, M.; Rao, M.S.; Hirt, A.M.; Wachs, I.E.; Deo, G. Oxidative dehydrogenation of propane over supported chromia catalysts: Influence of oxide supports and chromia loading. *J. Catal.* **2002**, *211*, 482–495. [[CrossRef](#)]
121. Rao, T.V.M.; Zahidi, E.M.; Sayari, A. Ethane dehydrogenation over pore-expanded mesoporous silica-supported chromium oxide: 2. Catalytic properties and nature of active sites. *J. Mol. Catal. A Chem.* **2009**, *301*, 159–165. [[CrossRef](#)]

122. Hakuli, A.; Kytökivi, A.; Krause, A.O.I. Dehydrogenation of i-butane on CrOx/Al₂O₃ catalysts prepared by ALE and impregnation techniques. *Appl. Catal. A Gen.* **2000**, *190*, 219–232. [[CrossRef](#)]
123. Liu, L.; Li, H.; Zhang, Y. Effect of synthesis parameters on the chromium content and catalytic activities of mesoporous Cr-MSU-x prepared under acidic conditions. *J. Phys. Chem. B* **2006**, *110*, 15478–15485. [[CrossRef](#)] [[PubMed](#)]
124. Santhosh Kumar, M.; Hammer, N.; Rønning, M.; Holmen, A.; Chen, D.; Walmsley, J.C.; Øye, G. The nature of active chromium species in Cr-catalysts for dehydrogenation of propane: New insights by a comprehensive spectroscopic study. *J. Catal.* **2009**, *261*, 116–128. [[CrossRef](#)]
125. Weckhuysen, B.M.; Wachs, I.E.; Schoonheydt, R.A. Surface chemistry and spectroscopy of chromium in inorganic oxides. *Chem. Rev.* **1996**, *96*, 3327–3349. [[CrossRef](#)]
126. Burri, A.; Hasib, M.A.; Mo, Y.H.; Reddy, B.M.; Park, S.-E. An Efficient Cr-TUD-1 Catalyst for Oxidative Dehydrogenation of Propane to Propylene with CO₂ as Soft Oxidant. *Catal. Lett.* **2018**, *148*, 576–585. [[CrossRef](#)]
127. Park, S.-J.; Kim, K.D. Adsorption behaviors of CO₂ and NH₃ on chemically surface-treated activated carbons. *J. Colloid Interface Sci.* **1999**, *212*, 186–189. [[CrossRef](#)]
128. Michorczyk, P.; Pietrzyk, P.; Ogonowski, J. Preparation and characterization of SBA-1-supported chromium oxide catalysts for CO₂ assisted dehydrogenation of propane. *Microporous Mesoporous Mater.* **2012**, *161*, 56–66. [[CrossRef](#)]
129. COSIA. \$20M NRG COSIA Carbon XPRIZE Finalists Announced; Teams Ready to Test Transformative CO₂ Technologies at Alberta’s Carbon Conversion Centre. Available online: www.cosia.ca/resources/newsreleases/20m-nrg-cosia-carbon-xprize-finalists-announcedteams-ready-test (accessed on 9 April 2018).
130. Zhang, D.; Wang, J.; Lin, Y.; Si, Y.; Huang, C.; Yang, J.; Huang, B.; Li, W. Present situation and future prospect of renewable energy in China. *Renew. Sustain. Energy Rev.* **2017**, *76*, 865–871. [[CrossRef](#)]



© 2020 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 (<http://creativecommons.org/licenses/by/4.0/>).