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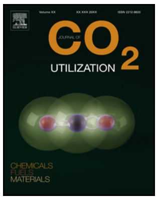

Review Article

CO_2 as a soft oxidant for oxidative dehydrogenation reaction: An eco benign process for industry

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ABSTRACT

Utilization of CO_2 as soft oxidant is emerging as a potential technology for industrial production of alkenes. Traditional way of alkene production in mass scale involves direct dehydrogenation of alkanes, which is energetically expensive. Oxidative dehydrogenation in the presence of CO_2 is a greener alternate to the traditional normal dehydrogenation process. Hence, this area has drawn remarkable investment of research interest worldwide. From environmental point of view, utilization of CO_2 is accepted as a means to mitigate the ever increasing greenhouse gas effect. CO_2 utilization is also attractive for its abundant availability and cheaper cost. But utilization of CO_2 suffers from the limitation of its inherent inertness. Application of suitable catalyst can help to overcome the thermodynamic and kinetic barrier of CO_2 activation. Exploitation of the soft oxidant property of CO_2 with the help of suitable catalyst in commercial scale can give a boost to polymer and fuel economy. Hence, it is interesting to focus on the possibilities of CO_2 utilization in oxidative dehydrogenation process. The challenges met in this process and the invention of catalytic technologies to address those problems are summarized in this mini-review.

Contents

1. Introduction

Carbon dioxide (CO_2) has acquired the focus of global chemical research community due to its large scope of industrial utilization. The abundant availability, non-toxic nature, and mild oxidizing property have made CO_2 chemistry more interesting. At present,

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industrial use of carbon dioxide can be found in production of chemicals, refrigeration systems, inert agent for food packaging, beverages, welding systems, fire extinguishers, water treatment processes, fertilizers, and many other smaller-scale applications. Large quantities of carbon dioxide are also used for enhanced oil recovery, particularly in the United States. Carbon dioxide can also become the raw material for producing carbon-based fuels. Biomass conversion to fuels also falls into the category of generating fuels from CO_2.

While talking about CO_2 chemistry, however, one can't escape from mentioning its environmental contributions. Carbon dioxide (constitutes 0.04% of earth's atmosphere) is an integral part of the 'carbon cycle' in which carbon flows in the form of energy and nutrient throughout the ecosystem and is exchanged between ocean, rock, soil, and biosphere, which is essential to maintain life on earth. CO_2 is also important in maintaining Earth's temperature through its natural greenhouse effect. However, this environmental boon has been regarded as one of the key culprits causing global warming. Excessive rise of atmospheric CO_2 level in the industrial era has resulted in the phenomenon of global warming, which has become a serious concern worldwide. Along with checking the CO_2 emission level, utilization of CO_2 has also been globally envisioned by the scientific community as an obvious means to diminish atmospheric CO_2 level. Active research groups are exploring new or improved CO_2 utilization processes. Accordingly, extensive literature is also present which deal with CO_2 uses in the industry [1,2].

Invention of novel pathways for utilization of CO_2 is well appreciated area in industrial as well as academic research. Application of CO_2 as a feedstock for production of fuels, and other useful products like cement, polycarbonate plastics, etc has gained substantial research focus. Mineralization of CO_2 and enhanced oil/gas recovery are some of the path breaking ways of controlling the ever rising CO_2 level. CO_2 has also found application in oxidation reactions as solvent in supercritical state and expanded solvent system. However, use of CO_2 as a soft oxidant is another small but important research area. The use of CO_2 as a mild oxidant, an O-transfer agent, or an H-acceptor offers some interesting challenge to heterogeneous catalysis because of high thermodynamic stability and kinetically inertness of the CO_2 molecule. Early studies on the use of carbon dioxide as a mild oxidant have been reported for syngas production from methanol [3–5]. Later on, CO_2 oxidation studies have been reported for ethylbenzene to styrene conversion by Sugino et al. [6] and have been investigated further by other research groups at length [7–21]. Oxidative dehydrogenation of the light alkanes has also been reported contemporarily [8]. Park et al. have deeply investigated different heterogeneous catalytic systems for utilization of CO_2 as a soft-oxidant. Apart from soft oxidant, CO_2 has also found application as a co-oxidant [9]. CO_2 has also found application in the oxidation reactions as solvent in supercritical state and expanded solvent system. Park et al. have reviewed utilization of CO_2 as a soft oxidant and promoter in 2012 [21], providing an in depth analysis of the role of CO_2 in soft oxidation process, factors responsible for activation of CO_2, and earlier relevant literature reports. Hence, this perspective will mainly emphasize on the recent literature reports. Firstly, a brief summary of CO_2 participation and activation will be reviewed followed by an in depth discussion of recent literature reports. Hopefully, this compendium will be helpful to further progress in this area in the right direction.

2. Participation of CO_2 as soft oxidant in dehydrogenation reactions: advantages versus challenges

Against normal dehydrogenation reaction, oxidative pathway is favoured due to constant regeneration of the catalyst active sites by the oxidants. During catalytic dehydrogenation reaction in the absence of an oxidant, the lattice oxygen of the catalyst participates in H_2 abstraction forming water. After the lattice oxygen of the catalyst surface gets exhausted, rate of formation of water decreases with a gradual increase in the formation of molecular H_2, which in turn slows down the process [10]. Removal of H_2 can overcome the equilibrium limitation and enhance catalytic performance [11]. However, in the presence of CO_2 the dehydrogenation reaction pathway changes in oxidative manner, in which CO_2 constantly maintains the supply of lattice oxygen and suppress the formation of molecular H_2. The presence of CO_2 induces reverse water–gas shift ($CO_2 + H_2 \leftrightarrow CO + H_2O$), which in turn favours the ODH reaction [12]. A schematic diagram of the oxidative dehydrogenation pathway is presented in Fig. 1.

CO_2 has several advantages as soft oxidant over various oxidizing agents tested for oxidative dehydrogenation like dry air, O_2, CO_2, N_2O, and SO_2 [13]. Being milder than O_2 and H_2O, CO_2 avoids the burning of valuable hydrocarbons [14], and therefore can be efficiently utilized in a soft oxidation process [15]. It is less hazardous than N_2O and SO_2 [16]. Apart from that, loss of latent heat does not take place, because CO_2 stays gaseous throughout the reaction [17]. Heat capacity of CO_2 is the highest among the typical gases [18,19]. CO_2 increases the selectivity by poisoning the non-selective site of the catalyst, which are responsible for formation of by-products [20]. Furthermore, CO_2 participates in the decoking process ($C + CO_2 \rightarrow 2CO$) that helps to sustain stable activity of the catalyst. Hence, the ODH reaction in the presence of CO_2 can generally be coined as a gas-mediated modification of the catalyst surface, which cause favourable influence on adsorption, diffusion, and redox properties of the catalyst to carry out the dehydrogenation of alkanes [21].

In spite of several advantages, utilization of CO_2 in soft oxidation processes face difficulty due to inertness of CO_2 molecule. The foremost challenging part of CO_2 utilization is the activation of CO_2 molecule. Gibbs energy of formation of CO_2 ($\Delta G^{\circ}_{298.15K} = -394.4\,\mathrm{kJ\,mol^{-1}}$) is considerably high. Kinetic barrier also plays a key role for its inertness. Interaction of CO_2 molecule with a metal complex in homogeneous reaction or with a solid surface in heterogeneous reactions helps to overcome the kinetic barrier. In nature, CO_2 fixation occurs through photosynthesis. The surface of the enzyme ribulose 1,5-biphosphate carboxylase/oxygenase gets involved in the process of CO_2 activation. It is well-established that the active site of CO_2 activation in photosynthesis is a Mg(II) ion embedded in a complex ligand field with oxygen atoms directly coordinated to the Mg centre. From the natural process of photosynthesis, it can be realised that sensible use of proper catalytic system can enhances the use of CO_2 as a useful reactant.

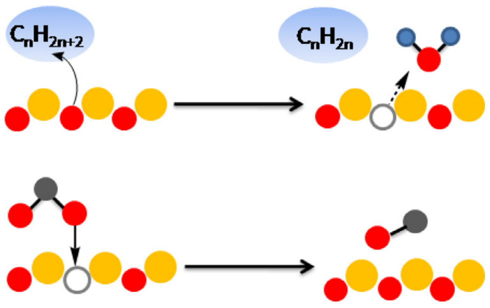

Fig. 1. Oxidative dehydrogenation pathway of alkanes to alkenes [●- metal, ●- oxygen, ●-carbon, ●- hydrogen].