

CARBON DIOXIDE TO VALUE ADDED CHEMICALS: A DREAM OR REALITY?

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1 Introduction

This is a common question in scientific endeavour, especially a new invention does not yield the desired results in an expected time period. For example, Photoelectrochemical decomposition of water was demonstrated in 1972 [1] which showed the possibility of hydrogen as an alternate for fossil fuels but the process efficiency could not reach the desired commercial stage in the next decades and this frustration led to this question [2]. In our anxiety for comfortable life style, search for economically viable alternate energy source within the existing infrastructure is one of the prime objective of scientific research. In this context, the conversion of carbon dioxide (the main product of fossil fuel combustion) assumes importance from various points of view. Among these reasons, the increased global warming has assumed significance. The relevance of the conversion of carbon dioxide to value added chemicals (a process of completing the carbon cycle) in relation to standard of life style has also been indicated [3]. In this context, the scientific effort for carbon dioxide capture and conversion have assumed a significance [4]. However, till today, these efforts have not yet yielded the desired results in terms of conversion levels, or fundamental understanding of the catalytic (different catalytic processes like photo-catalytic, photo-electrochemical electro-chemical, and other combinations) processes, thus there is an urgent need to address this issue with a view to postulate the suitable conditions for this process [5]. There are other challenges in making this process commercially viable. Among these, the conversion levels and the selective product distribution achieved, choice of catalytic material, the choice of the feed composition have been receiving attention.

The basic understanding of the activation of carbon dioxide on the catalyst surface is matter of contention. The issue is which of the two centres of the reactant molecule has to be activated on the surface of the catalyst? The surface intermediate(s) that are formed on the activation of carbon dioxide is oxygenated or not since the formation of hydrocarbons depend on carbide type surface species. It may be postulated that metal centres may activate carbon centre while anion (oxide) centres may prefer adsorption through oxygen centre of the molecule.

In view of these concerns, in this short presentation, few of these aspects are addressed in brief.

2 The Choice of Reaction Conditions

The catalytic reduction of carbon dioxide can be carried out in presence of H_2 , H_2O , or CH_4 or alone. If carbon dioxide alone is used one needs subsequent Fischer Tropsch process for the formation of hydrocarbons. From free energy considerations, it is preferable to use carbon dioxide with a co-reactant.

The conversion of carbon dioxide can yield either CO or other hydrocarbons like methane, or methanol etc.

The values of free energy of formation of a few species involved in the reduction of carbon dioxide are given in Table .1.

The points that one can derive from the values of free energy are:

chemical species	Gibbs free energy of formation in kJ/mol
C ₈ H ₁₈	17.3
C ₁₀ H ₂₂	34.4
Dinitrogen	0.0
Hydrogen molecule	0.0
Oxygen	0.0
Ammonia	-16.6
Methane	-50.7
Ethane	-32.9
Propane	-23.6
Carbon monoxide	-137.15
Methanol	-159.2
Water	-228.4
Carbon dioxide	-394.0

Table 1: Gibbs free energy of formation of selected chemicals in relation to carbon dioxide reduction

1. Carbon dioxide is a very stable molecule compared to other reduction products that are possible
2. Converting carbon dioxide to carbon monoxide is not very favourable as compared to the formation of other reduction products.
3. Carbon dioxide reduction in presence of molecular hydrogen should be preferable.
4. The conversion of carbon dioxide is facile if it is used as a co-reactant with other substances that have higher Gibbs free energy for example H₂ or CH₄.
5. Thermal dissociation of carbon dioxide to carbon monoxide involves nearly -293 kJ/mol as compared to Carbon dioxide reacting with hydrogen to give CO and water is only 51 kJ/mol

- It appears that self decomposition of carbon dioxide to give carbon monoxide which is utilized in further Fischer Tropsch process is not that preferable when compared to use carbon dioxide as co-reactant with water, methane or hydrogen to produce hydrocarbons.
- It is also possible to achieve required selectivity with respect to hydrocarbon, based on thermodynamic data.
- These postulates are based on thermodynamic considerations and the kinetics of the process can still be demanding.

Next, one can visualize the activation of carbon dioxide on the surface of a catalyst. There are various forms of surface carbon dioxide species. On oxide surfaces, carbonate type species can also exist. The free carbon dioxide molecule can attach with carbon centre to the metal (or cation) site while the oxygen centre will be adsorbed on the anion species. Successive adsorption of carbon dioxide through oxygen centre will give surface carbide species which will hydrogenate and produce hydrocarbons. Surface hydrogen species produced from the co-reactant (H₂, H₂O or CH₄) can be utilized for hydrogenating the surface carbon species. (see Fig.1.). The dissociation of C - O bond can be facilitated by the presence of adsorbed hydrogen species at adjacent sites which will result in surface hydroxyl type species which can be desorbed as water. The charge transfer should be in the opposite directions from oxygen end and to the carbon end with respect to the surface. In this way the charge density on carbon centre will be suitable for carbide species formation and thus the route to hydrocarbon is facile.

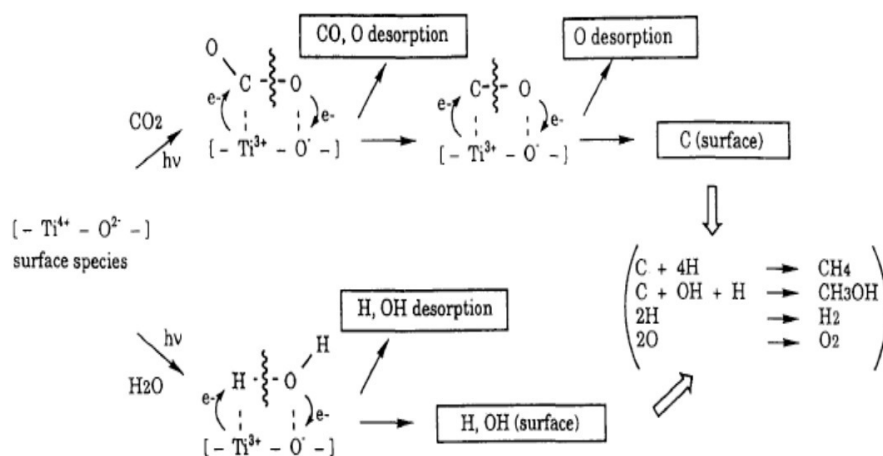


Figure 1: Schematic presentation of the photo-catalytic reduction of carbon dioxide with typical co-reactant water on the surface of titanium dioxide catalyst (From ref 6)

3 References

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