A conceptual formulation of photochemical CO2 reduction catalyst system

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In a recent publication [1] the photosynthetic conversion of CO2 to hydrocarbons ( methane and other higher hydrocarbons) on Pd /TiO2 in conjunction with nafion has been reported. However, the photo conversion efficiency of the process is very low because the activation of the thermo chemically most stable CO2 requires highly energetic electrons. Since the one-electron reduction of CO2 +( the initial step in the reduction process) requires high potentials of the order of 2 Volt, a more favorable pathway is to reduce CO2 though proton-coupled multiple-electron transfers (PCET). Nafion (per fluorinated polymer with sulfonate groups) coated Pd–TiO2 particles (Nf/Pd–TiO2) were prepared and their reactivity for the photo reduction of CO2 was tested. The role of the Nafion layer is to enhance the local proton activity within the layer to facilitate PCET reactions and to stabilize intermediates and to inhibit the re-oxidation of the CO2 reduction products. Nf/Pd–TiO2 is more active than Pd–TiO2 for the photo-production of hydrocarbons (e.g., methane, ethane, and propane). The photosynthetic activity of the Nf/Pd–TiO2 catalyst was maintained through repeated cycles of photoreaction, which confirms the stability of the Nafion layer. The proposed Nf/Pd–TiO2 should serve as a model of more practical catalysts for the artificial photosynthesis that is based on PCET reactions.

The conceptual design of the catalyst system employed in this study is shown in Fig [This figure is reproduced from this paper]

 

Fig.1 Pd/TiO2 on Nafion catalyst system for the photochemical reduction of CO2 [from ref 1]

In the light of this communication, the following is presented for conceptual analysis and possible adaptation. Essentially the points of relevance are:

1. A direct proton source rather than from the decomposition of water is desirable so that the reduction of CO2 is facilitated.
2. It must be ensured that the species employed for proton source should not undergo any electrochemical reaction within the potential range for CO2 reduction reaction.
3. The reactivity of the proton should be as high as that in Nafion, where the Proton is in a highly electronegative environment of Fluorine atoms.
4. The available protons should be capable of reacting with carbon dioxide directly promoted by the light absorbed in TiO2 and reduction reaction should be carried out on some reactive metal sites.
5. In order to overcome the low solubility of CO2 the source is any carbonate which can in situ generate CO2  and thus can sustain source.

Considering these aspects and also based on argumentative formulations it is possible that alternate PCET catalyst support systems which may sustain more acidic protons can be tried like heteropoly acids or super acids like sulphated zirconia.

Reference

[1] Wooyul Kim et al., Energy Environ. Sci., 5, 2012, 6066