Input Power-Dependent Low-Temperature Plasma-Assisted Catalytic Hydrogenation of Carbon Dioxide to Propane, Methanol, and Butane over Iron-Doped Cobalt Catalyst

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Abstract

Figure 1. Cold plasma in a coaxial reactor

Concern regarding climate change and depletion of fossil fuel resources have necessitated the development of sustainable and clean technologies for carbon dioxide (CO_2) utilization. As many industries such as power and manufacturing plants, produce carbon dioxide as a primary output or byproduct, there is interest and significant financial incentive in the effective capture, conversion, and utilization of CO_2. The reaction between CO_2 and H_2, known as carbon dioxide hydrogenation, may yield mainly methane (CH_4), carbon monoxide (CO), or hydrocarbons such as gaseous C_2-C_6, liquid oxygenates, water, methanol, and ethanol. Recently, studies have shown that the combination of select catalysts and supports used in addition to an applied low-temperature dielectric-barrier discharge plasma not only activates thermodynamically-stable CO_2 molecules, but also augments catalytic reactions to increase favorable product selectivity at relatively low power. Previous studies have focused on methane and ethane; however, propane (C_3H_8), methanol (CH_3OH), and butane (C_4H_{10}) are much more valuable products. Although many catalysts and support combinations have been studied, reported propane and butane selectivity remain low and uncontrollable. Additionally, to the best of our knowledge, no reports showing a catalyst and support combination that enables swift transition to methanol production. Thus, in this work, we have investigated plasma-catalytic CO_2 hydrogenation over 1Fe-14Co/γ-Al_2O_3 catalyst, Al_2O_3 , and TiO_2 support combinations to show that the selectivity of higher hydrocarbons can be controlled with input power, a suitably high dielectric constant, and applied voltage.

Significance & Introduction

$$CO_2\,(g) + 4\,H_2\,(g) \rightleftharpoons CH_4\,(g) + 2\,H_2O\,(g)$$
$$CO_2\,(g) + 3\,H_2\,(g) \rightleftharpoons CH_3OH\,(g) + H_2O\,(g)$$
$$CO_2\,(g) + H_2\,(g) \rightleftharpoons CO\,(g) + H_2O\,(g)$$
$$n\,CO\,(g) + (2n+1)\,H_2\,(g) \rightarrow C_nH_{2n+2}\,(g) + n\,H_2O\,(g)$$
$$n\,CO\,(g) + 2n\,H_2\,(g) \rightarrow C_nH_{2n}\,(g) + n\,H_2O\,(g)$$

Studies have shown that the combination of select catalysts and supports used in addition to an applied low-temperature dielectric barrier discharge plasma not only activates thermodynamically-stable CO_2 molecules but also augments catalytic reactions. Additionally, the product selectivities can be changed by changing input power to the system.

Significance:

- Shows the significance of dielectric constant of the support material in changing discharge characteristics
- Shows the effect of applied voltage change
- Propose dominant reaction pathways for propane, butane, and methanol production

Setup

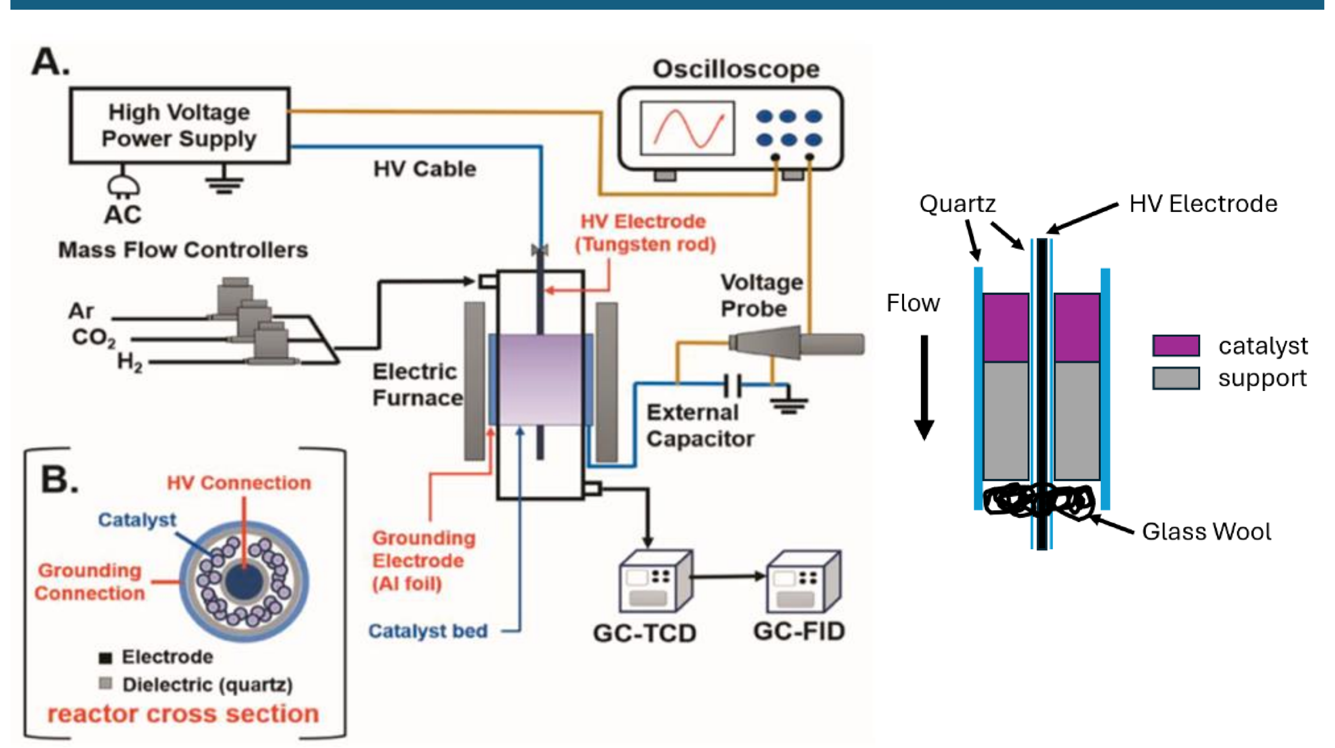


Figure 2. Schematic of the experimental setup, catalyst bed configuration, and support pellet size of 0.5-1 mm

Results

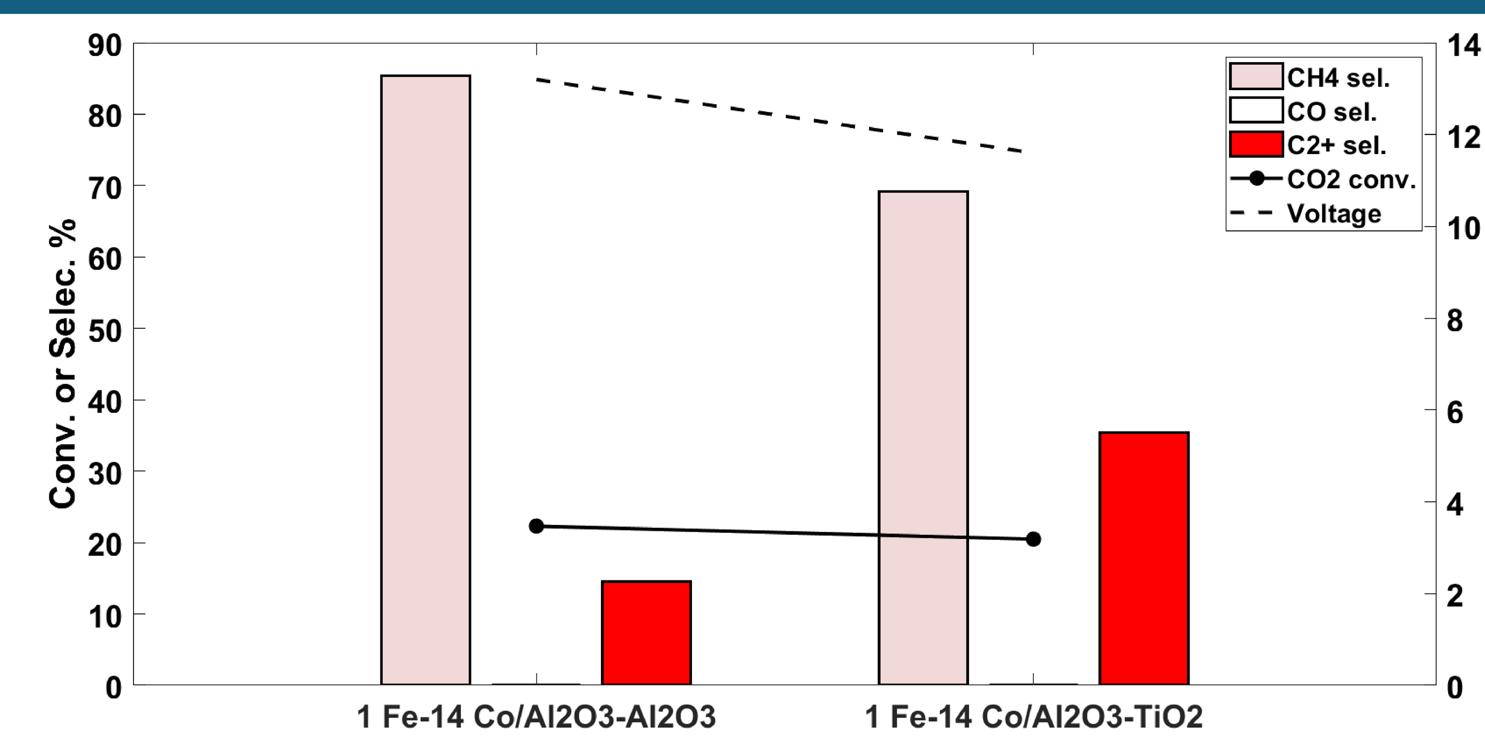


Figure 3. CO_2 conversion, product selectivity, and steady-state voltages of select iron and cobalt loadings compared with titania support. Reaction conditions: H_2 /CO_2 = 3 in argon balance, flow rates = 80,10 mL min^{-1} P = 1 atm, frequency = 23.5 kHz

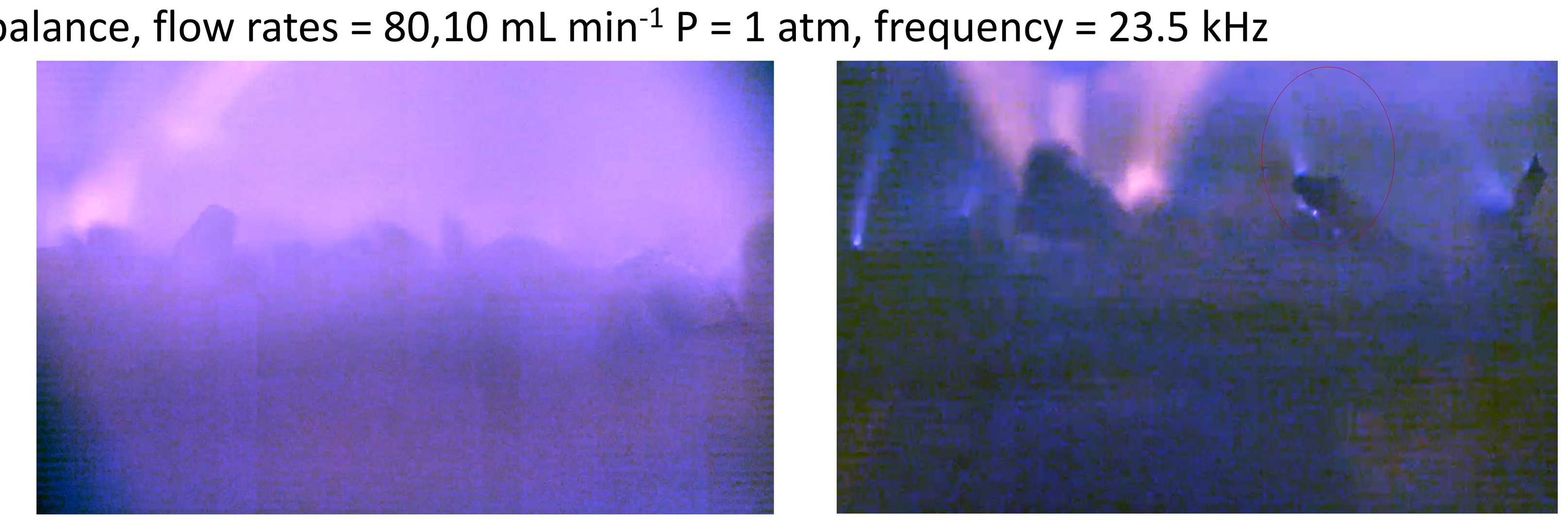


Figure 4. Discharge on γ-alumina ($\varepsilon_r \approx 3.3$) on the left and titania ($\varepsilon_r \approx 81$) on the right

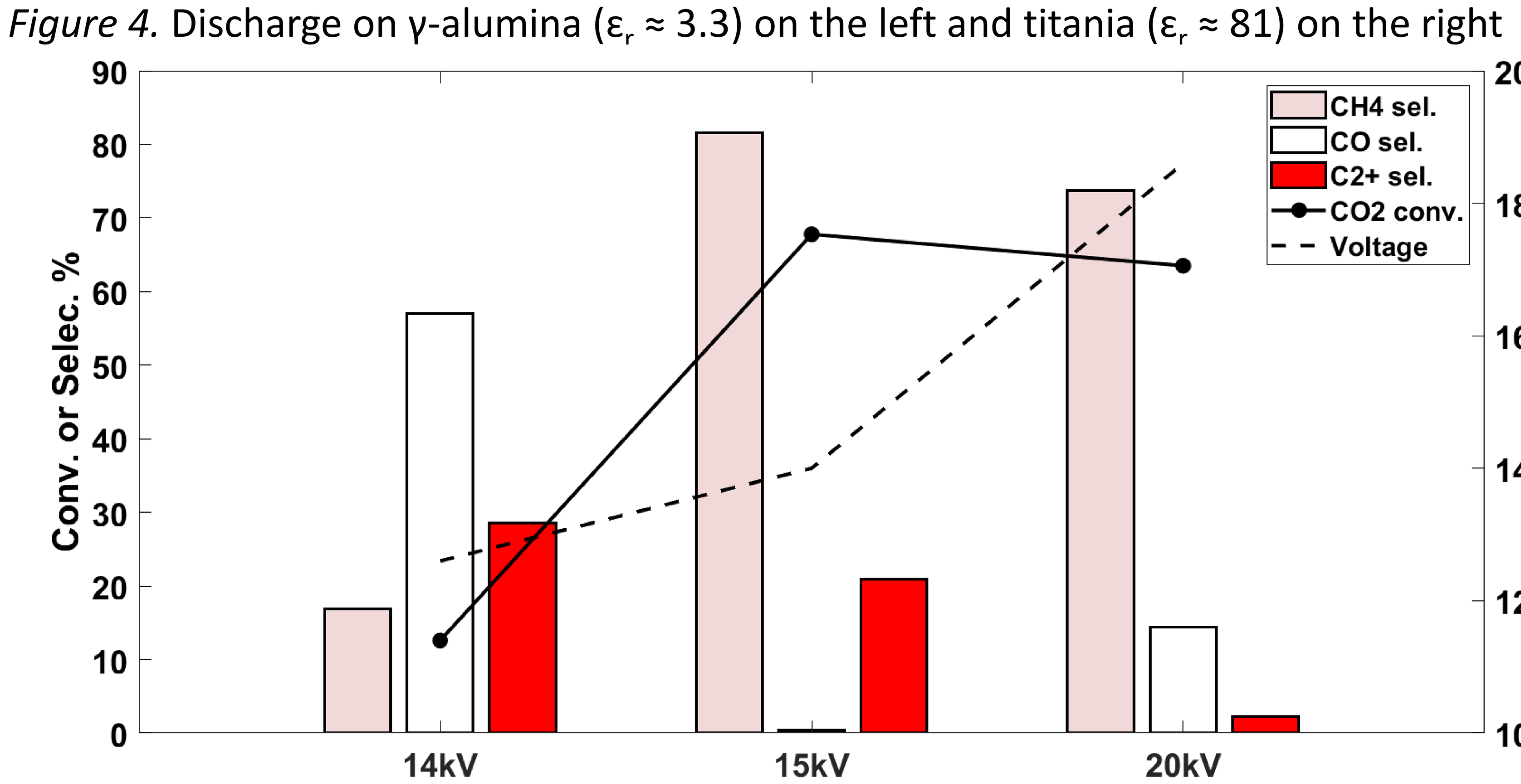


Figure 5. Effect of applied voltage change on 1%Fe-14%Co/TiO_2 catalyst support combination. Off the wall Power readings 19.6, 23.4, and 36 W respectively.

Proposed Mechanism

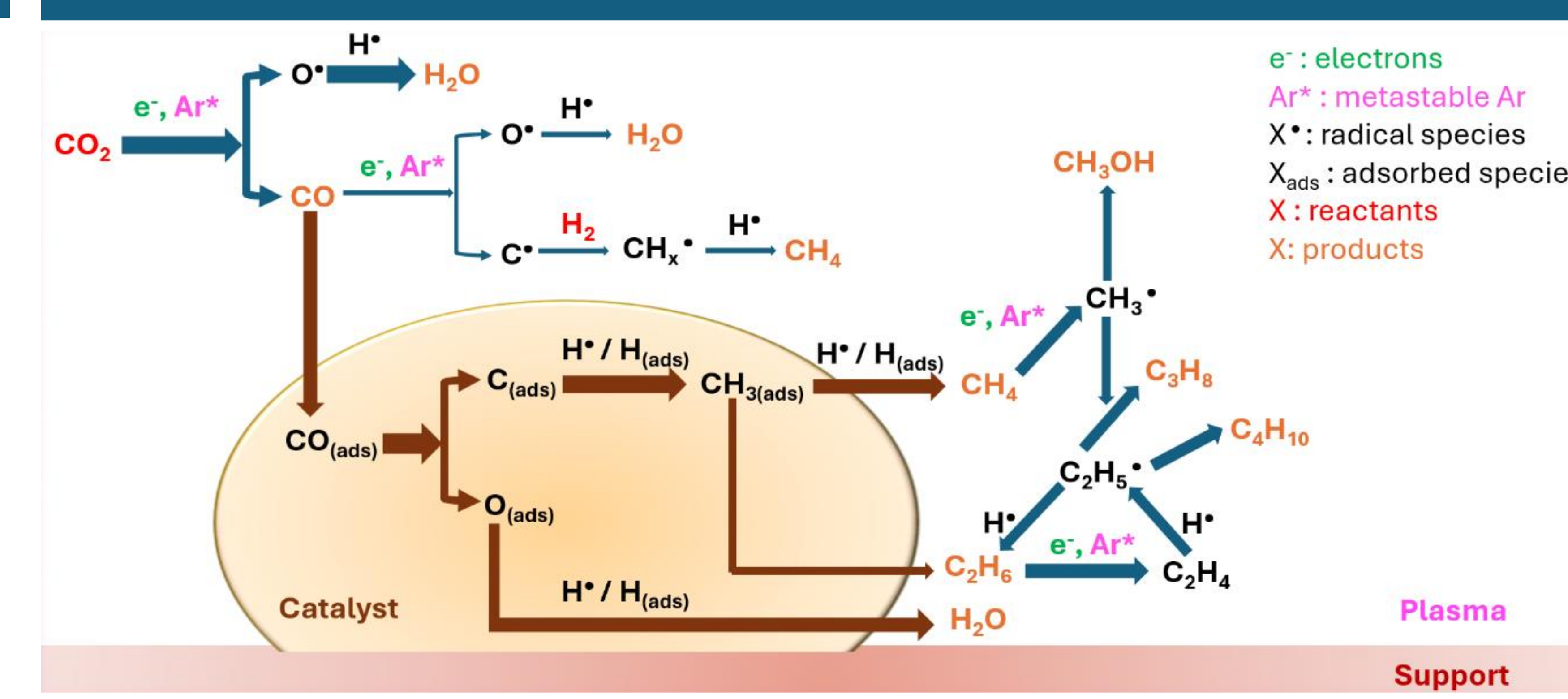
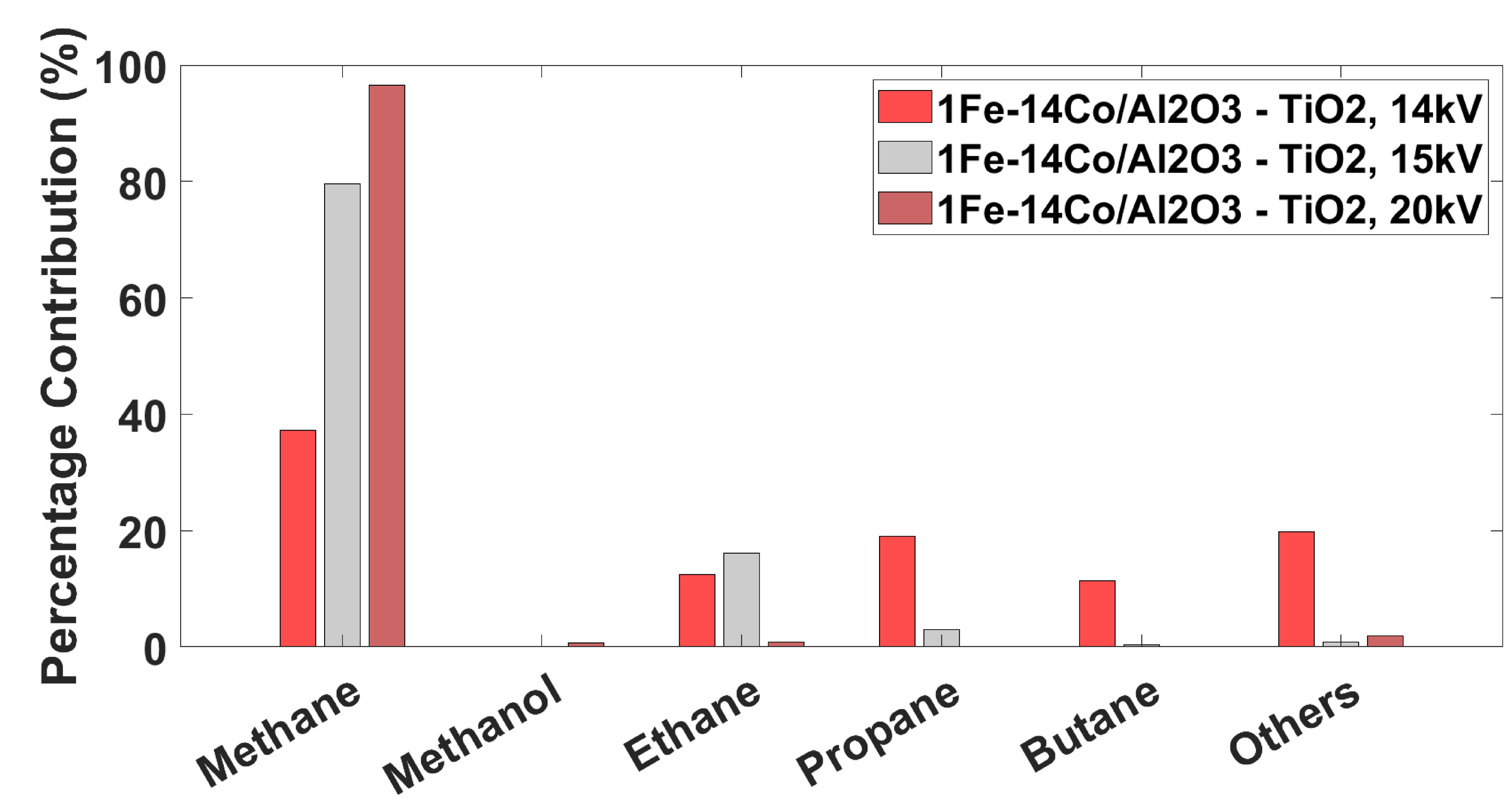


Figure 6. Dominant propane formation pathway showing CO adsorption on the catalyst

Hydrocarbon Distribution



Summary

LTP-driven catalytic process for the conversion of CO_2 and H_2 into higher hydrocarbons with an increase in propane selectivity over ethane. We show the significance of the dielectric constant of the support material and the effect of applied voltage change

Acknowledgment

1. Propane Education & Research Council
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