**CO2 Hydrogenation to Methanol Using Cu/ZSM-5 Extrudates in a Cold DBD Plasma.**

Maxwell Quezada1, Federico Azzolina-Jury2, Isabelle Polaert1, Alain Ledoux1, Christian Fernandez2

*1 Normandie Univ, UNIROUEN, INSA Rouen, LSPC, Laboratoire de Sécurité des Procédés Chimiques 76000 Rouen, France*

*2 Normandie Univ, ENSICAEN, UNICAEN, CNRS, LCS, Laboratoire de Catalyse et Spectrochimie, 14000 Caen, France*

*\*Corresponding authors:* *Isabelle.polaert@insa-rouen.fr**;* *Federico.azzolina-jury@ensicaen.fr*

**Highlights**

* Preparation and optimization of Cu-ZSM-5 and Cu-Al2O3 extrudates catalysts
* Complete characterization of porous extrudates catalysts
* DBD Plasma-assisted low temperature methanol production from CO2 hydrogenation
* Efficiency comparison between plasma and conventional catalysis in the CH3OH production

**1. Introduction**

 Carbon dioxide is one of the main greenhouse gases (after water vapor) and also an abundant source of C1. CO2 is a non-toxic, non-corrosive, nonflammable molecule [1] and very stable thermodynamically, requiring thus large amounts of energy for its dissociation. CO2 is produced from almost all combustion processes causing an increase in the world average temperature. To prevent its release into the atmosphere, one of the existing technologies is the capture and storage of CO2 in underground reservoirs [2], but this does not benefit from this potential carbon source. A more valuable technology could be the chemical recovery of this captured CO2 by its valorization into hydrocarbons, more specifically its chemical transformation into methanol.

CO2 hydrogenation to methanol is accompanied by the reverse water-gas-shift (RWGS) reaction, which produces CO. These reactions have been well studied in the literature and two main problems have been detected: the important amounts of energy required for breaking the CO2 bonds, and catalysts needing fairly high temperatures for activating the CO2 molecule, both situations favoring the undesired RWGS reaction.

To address these problems, we propose a new catalytic process using copper catalysts synthetized on various supports and used in a cold DBD plasma reactor. This original technique allows to work at atmospheric or under moderate pressure and favoring methanol production.

**2. Methods**

We have first developed our own catalyst Cu/NaZSM-5 and compared it to Cu/Al2O3. These catalysts are in the form of cylindrical extrudes of 5 mm x 3 mm, aiming to deliver results closer to industrial exploitation. In the literature, little research has been done on the use of the sodium form of the ZSM-5 to produce methanol [3]. A green template-free process to synthesize NaZSM-5 is used in this work. All corresponding characterization analyses have been conducted for the supports (N2 physisorption, pyridine adsorption and XRD) and for the catalysts as well (N2 physisorption, pyridine adsorption, H2 chemisorption, CO adsorption, ICP, TPR and XRD).

Second, we have performed experiments using a non-thermal plasma reactor, which is able to activate the CO2 molecule at room temperature and atmospheric pressure, increasing the CO2 dissociation rate in gas phase and the methanol yield over catalysts. All experiments were performed with a molar ratio of H2/CO2 = 3 using argon as a vector gas to increase the dissociation rate of CO2, inside of a dielectric barrier discharge reactor using Cu/Al2O3 and Cu/NaZSM-5 as catalysts, in parallel with a classic fixed-bed configuration in order to compare their catalytic performances in terms of methanol production.

**3. Results and conclusions**

Catalysts extrudates were successfully prepared, and their preparation was optimized. It was observed that there is an ideal range for the HNO3/boehmite molar ratio (between 19 and 37) where reducibility and dispersion of the copper present on the catalyst were improved when compared to the acid-free catalysts. Also, the addition of HNO3 improves the strength of the Lewis’ acidic sites at temperatures higher than 200 °C, which are the usual reaction temperatures for the conventional fixed bed reactors.

First results have been obtained showing that methanol is produced when using both Cu/Al2O3 and Cu/ZSM-5 catalysts under cold DBD plasma at atmospheric pressure. The plasma assisted catalytic tests were evidenced to be more efficient than the conventional ones and a clear improvement was observed in terms of methanol yield and CO2 conversion. A schema of the reactor is shown below:

**Figure 1.** Cold plasma DBD reactor used for CO2 hydrogenation into methanol.

**References**

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