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Study on the mechanism of plasma-assisted CO_2 methanation over Ru-zeolite catalysts in a DBD *operando* FTIR cell.

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ABSTRACT FOR ORAL COMMUNICATION

CO_2 methanation is a well-known reaction that is advantageous in using CO_2 as a building block in the production of fuels, thus contributing to mitigate greenhouse gases emissions and fight the issues tied to climate change [1]. The traditional thermal pathway requires the use high temperatures to activate the reaction, which could cause several drawbacks.

An alternative for using thermal energy is the use of an energy source capable of activating the reactants at low temperature: non-thermal plasmas. In the last decade, a new branch of plasma science has been emerging: plasma-catalysis, whose objective is to enhance catalytic reactions by adding a plasma to the reaction cycle [2].

Of particular interest is the utilisation of atmospheric dielectric barrier discharge plasma-induced catalysis, aiming at increasing products yield (by modifying energy barriers of catalytic pathway) with simultaneous low power consumptions [3]. Although promising, this novel approach poses unknown and critical aspects concerning the design of the catalyst and its interactions with plasma [4].

Consequently, in the present work different Ru-based zeolite supported (BEA, MOR, ZSM5, USY) catalysts were prepared to study their behaviour in a DBD plasma-catalytic setup, allowing to observe how different properties of the catalyst can affect the reaction pathway. A novel atmospheric pressure DBD *in-situ operando* transmission FTIR cell was designed and utilized to follow the formation of different species in the plasma and at the surface of the catalyst during the CO_2 methanation reaction, carried out at atmospheric pressure and varying frequencies (0-5 KHz) and discharge voltages (0-25 kV).

To compare different reaction pathways and to discriminate between plasma-induced heating and other effects of the plasma, the same catalysts were also tested in a thermal *in-situ operando* cell. The catalytic activity of the samples (figure 1) was studied in both thermal (packed bed laboratory-scale unit: 86100 mL g_{cat}^{-1} h^{-1}, P_{CO2} = 0.16 bar, H_2/CO_2 = 4:1, 200-450 ºC) and plasma catalysis (packed bed DBD reactor).

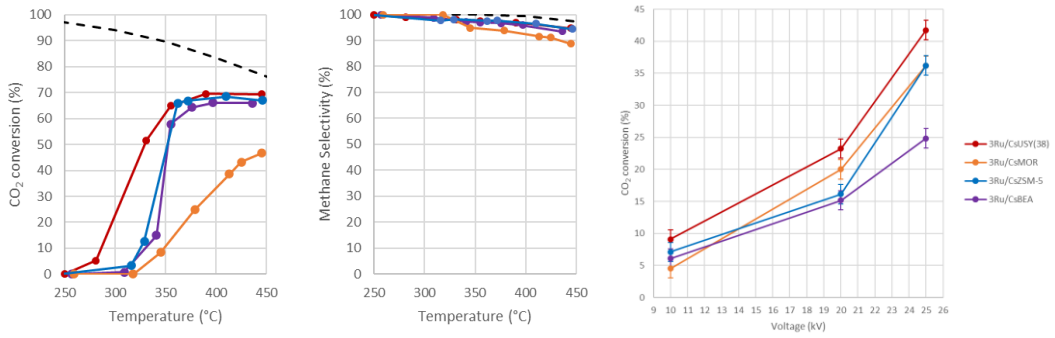

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Figure 1 – a) catalytic activity of the studied samples in thermal catalysis in terms of CO_2 conversion and methane selectivity as a function of the temperature; b) catalytic activity of the studied samples in plasma catalysis in terms of CO_2 conversion as a function of the applied voltage.

CO was found to be the main product of the reaction coming from CO_2 dissociation by plasma in the gas phase. CO_2 is also vibrationally excited by the plasma, facilitating its adsorption on the surface of the Ru catalysts in the form of oxidized carbon species (formates, aldehydes, carbonates, carbonyls…) that are then progressively hydrogenated to methane. Adsorption and surface reaction of key intermediates (namely formate and aldehydic groups) are observed even on the support alone, an occurrence not reported before for thermal catalysis (figure 2).

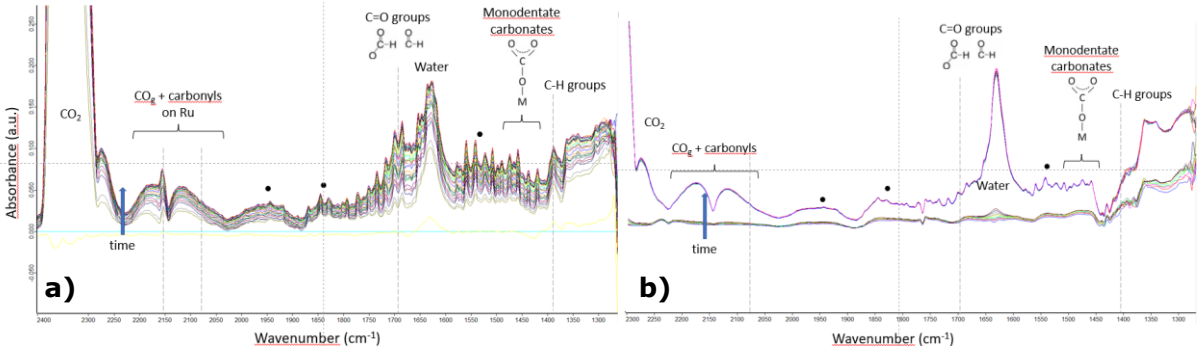

Figure 2 – Subtraction spectra in the 2400-1300 cm^{-1} spectral region acquired via *operando* FTIR during the DBD-assisted CO_2 methanation reaction over Ru-impregnated catalyst (a) and support alone (b).

Thus, a detailed mechanism for DBD-assisted CO_2 methanation is proposed (figure 3).

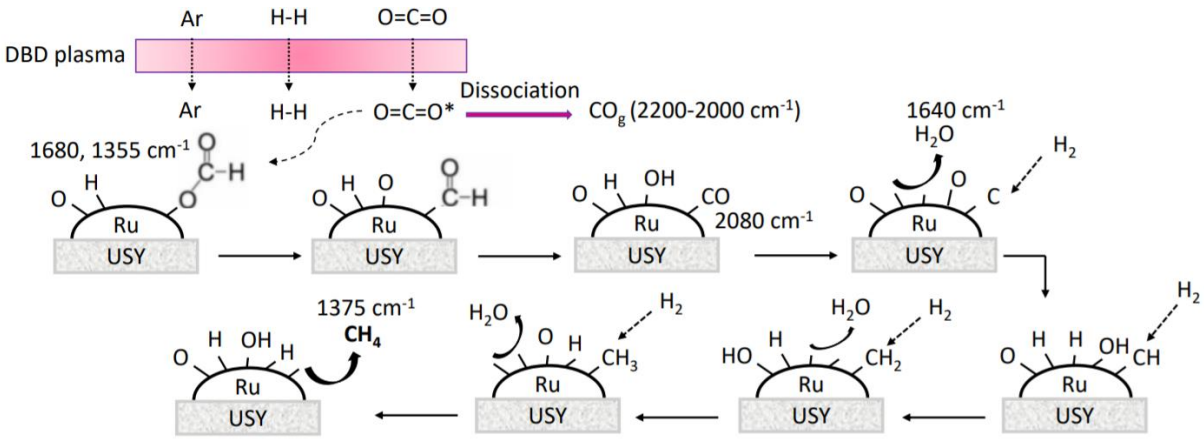

Figure3 – Proposed mechanism for DBD-assisted CO_2 methanation over Ru-impregnated USY zeolite.

Submission in the scope of topic 1: ***Fundamentals and mechanisms of CO_2 plasmas interacting with surfaces.***

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