Ru-based catalysts for plasma-assisted CO2 methanation

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Abstract
In this work, novel catalysts to carry out the plasma-assisted CO2 methanation reaction (Sabatier reaction) were designed and tested. In fact, CO2 is a very interesting reactant in hydrogenation reactions because of its production by human industrial activity and the necessity to remove it from the atmosphere, where it acts as a greenhouse gas, while the produced CH4 has many advantages as well, including already having an existing distribution network. The traditionally thermally activated reaction could be further enhanced by the utilisation of Dielectric Barrier Discharge (DBD) plasma-induced catalysis in the presence of a catalyst material. Thus, different classes of Ru-based catalysts, supported over microporous zeolites (USY, BEA, MOR and ZSM-5) and mesoporous silicas (SBA-15 and MCM-41), were designed, synthesized and tested in both thermal and plasma-assisted catalysis conditions. Indeed, the catalyst prepared using 3% in weight of Ru dispersed by incipient wetness impregnation over USY zeolite having a Si/Al ratio of 38 and Cs as a compensating cation was found to be the best one in both environments, pointing out to many properties of the support material (hydrophobicity, basicity and porosity) to be critical in defining a well-performing catalyst. Moreover, a heavy focus on the reaction mechanism was put on this study, by means of in-situ operando FTIR, which was possible under plasma-catalysis conditions thanks to the design of a novel DBD Transmission-FTIR cell. The proposed mechanism, under plasma-catalysis conditions involves the dissociation of CO2 in the plasma and its adsorption on the surface of the catalysts as carbonates or carbonyls species, that are then progressively reduced to formates and then to methane. This mechanism is quite similar to the one observed under thermal catalysis conditions, likely due to the mild conditions (temperature) created by the DBD plasma, that nonetheless unlocks adsorption and reaction pathways happening on the supported material alone, not observed before.