Methane production by CO$_2$hydrogenation reaction with and without solid phase catalysis

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Abstract
Leveraging on the experience gained by designing and assembling a prototype experimental apparatus reusing CO\textsubscript{2} to produce methane in a reaction with H\textsubscript{2}, we are developing an alternative innovative cost effective and contaminant resistant synthetic strategy based on the replacement of the solid phase catalysis with a homogeneous gas phase process going through the forming CO\textsubscript{2}\textsuperscript{2+} molecular dications.

Keywords: methanation reactor; CO\textsubscript{2} waste; free methane; catalyst; plasma, dications.

Introduction
As reported during the 2\textsuperscript{nd} SMARTCATs general meeting of the COST Action CM1404 we are carrying out a research aiming at re-using CO\textsubscript{2} and implementing a validated laboratory technology based on an experimental prototype apparatus (called ProGeo) producing carbon neutral methane through the chemical conversion of CO\textsubscript{2} waste flue gases using renewable energies.
The research is being carried out in collaboration by researchers of the laboratories of the University of Perugia and of ENEA (the Italian National Agency for New Technologies, Energy and Sustainable Economic Development of Frascati) with the support of a cluster of Small and Medium-sized Enterprises (SME)s coordinated by the Master-up srl company. In particular, the project leverages a) on the expertise of the Departments of Chemistry, Biology and Biotechnology and of Civil and Environmental Engineering of the University of Perugia on the experimental and theoretical treatment of elementary reactive and non reactive molecular processes [1-8] and b) on the engineering capabilities of designing, building and experimenting innovative apparatuses of ENEA [9] researchers with the support of the above mentioned SMEs specialized in the field of molecular science software modeling. Such
collaboration has been incubated by the networking activities of some COST actions [10,11] and of some virtual communities of the European Grid Infrastructure EGI.eu [12, 13]. The first purpose of this paper is to illustrate how the developed distributed computing machinery (i.e. the collaborative (workflowed) sharing of high level accurate and approximate ab initio and empirical calculations of the electronic structure of the involved molecular systems, the fitting and, as an alternative, force field formulations of the related potential energy surfaces together with accurate quantum, quantum-classical, quasi-classical dynamical calculations of the detailed properties of the system plus their integration with statistical averaging of the detailed properties over the unobserved parameters as well as their combination in multi-scale treatments) has provided a solid ground for a converging comparison of experimental and computational investigations of the methane formation from CO$_2$ using solid state catalyzed processes.

The second purpose of the paper is to illustrate how the progress made in the above mentioned research line has prompted a new one based on the use of the Synchrotron and the Free Electron Laser light sources to investigate the possibility of developing routes alternative to solid state catalyzed techniques. In particular, details are given on how CO$_2$ hydrogenation can occur via plasma generation by either electrical discharges or by vacuum ultraviolet (VUV) excitations of a CO$_2$ + H$_2$ gas mixture.

Accordingly, the paper is articulated as follows:

in section 2 structure and performances of the methanation reactor are illustrated;

in section 3 the computer simulation of the involved processes is analysed;

in section 4 the research lines driving the evolution of the apparatus towards a pure gas phase one are discussed.
2. The present methanation reactor

Experimental measurements of methane yields of ProGeo have been carried out using CO$_2$ bottles (some measurements have been performed also using CO$_2$ produced (in the ratio of 1.9 kg per litre) from grapes fermentation of Marsala, a famous wine of the region where Garibaldi got ashore when starting the unification of Italy, kindly provided by IRVO (Istituto Regionale Vini e Oli)). The measurements show a complete compatibility with the catalyser used for the methanation process in ProGeo. The used catalyst is KATALCO$_{JM}$ 11-4MR a commercial product of the Johnson Matthey company (made of silicate hydrous aluminum, silicon oxide, nickel, nickel oxide, magnesium oxide, graphite porous small cylinders of average diameter 3.1 mm and height 3.6 mm containing metallic nickel) whose 2500X micrography is shown in Fig. 1.

The ProGeo reactor is designed for an exit CH$_4$ maximum flux of 1 Nm$^3$/h. As shown in Figure 2, it is articulated in twin columns (twin flow channels) externally cooled thanks to shared laminar elements in order to dissipate the heat produced by the exothermicity of the reaction ($\Delta H_{298K} = -164.9$ kJ mol$^{-1}$). Design parameters of the reactor are:

- GHSV (Gas Hourly Space Velocity) (ml h$^{-1}$ gr$^{-1}$) and SV (Space Velocity) (h$^{-1}$).
- Another useful parameter is the ratio between the total flux of gas and the exposed surface of the catalyser indicated as GHCS (Gas Hourly Catalyst Surface) (cm h$^{-1}$).
- The value of the reactor parameters of the present version of the ProGeo apparatus are: GHSV = 3200 ml h$^{-1}$gr$^{-1}$ and SV = 2100 h$^{-1}$ leading to a GHCS parameter of 155 cm h$^{-1}$.

The resulting features of the present ProGeo apparatus shown in Fig. 2 are:

- External diameter of the single channel 60 mm;
- Catalysed total length 660 mm;
- Maximum inlet flux (H$_2$+CO$_2$) 6 Nm$^3$/h;
- Reference Molar ratio (CO₂/H₂) 1/5;
- Maximum outlet flux (CH₄) 1 Nm³/h.

Experimental measurements have been carried out by varying:

- the CO₂/H₂ molar ratio from a minimum of 1/4 to a maximum of 1/5.5;
- the reactor temperature from a minimum of 220 °C to a maximum of 450 °C;
- the H₂ flux from a minimum of 0.8 Nm³/h to a un maximum of 2.5 Nm³/h;
- the pressure from a minimum of 1 bar to a maximum of 2 bar.

A key element for a quantitative measurement of the reaction yield is the regular monitoring of the temperature both along the central axis of each channel (maximum temperature) and along the peripheral axis (minimum temperature). In Figure 3 the location and labels of the channel thermocouples (6 axial and 3 peripheral) are shown as dots together with the cross section of the twin columns.

The methanation reactions occur mainly on the top segment of the reactor close to the inlet (90% in the first 200 mm). Accordingly, most of the produced heat is detected by the central thermocouples (T5, T6 and T14, T15). The average of the measured percentage of produced methane is plotted as a function of the molar ratio and temperature in Fig. 4. As is apparent from the Figure, the threshold temperature is 240°C and the range of temperature of optimal yield is 300 - 350°C. The molar ratio has a significant impact on the percentage of produced methane with the optimum value of the CO₂ / H₂ ratio being 1/5.

3. Computational simulation of methane production from the CO₂+H₂ reaction with solid phase catalysis

In our laboratory the initial rationalization of the processes involved in producing methane via the Sabatier reaction (i.e. by making H₂+CO₂ react on a catalytic surface [14]) has been
performed by following the flowchart of ZACROS [15], a Kinetic Monte Carlo (KMC) 
[16,17] software package written in Fortran 2003. ZACROS leverages on the Graph-
Theoretical KMC methodology coupled with both cluster expansion Hamiltonians for the ad-
layer energetics and the Brønsted-Evans-Polanyi relations for the activation energies of 
elementary events [16]. ZACROS enables researchers in the areas of Computational Catalysis 
and Surface Science to perform dynamic modelling of adsorption, desorption, surface 
diffusion, and reaction processes on heterogeneous catalysts. Although in our traditional 
GEMS (Grid Empowered Molecular Simulator) [18] approach based on distributed 
computing platforms the rates \( r \) of elementary processes are computed by running molecular 
dynamics calculations based on Potential Energy Surfaces (PES)s originating from \textit{ab initio} 
treatments, in the version of ZACROS implemented by us, for all the elementary steps 
potentially participating in the mechanism, the values of \( r \) to be used are taken from the 
literature and are usually given the following Transition State (TS) theory formulation [19,20]

\[
r = A \cdot \exp \left( -\frac{E_a}{k_B T} \right)
\]  

(1)

in which \( A \) is a pre-exponential factor (quantifying the propensity of the system to cross from 
TS to products) while the exponential term brings in the information on the PES of the related 
elementary process (either forward “f” or backward “b”) as the energy difference \( E_a \) between 
the stationary point of the potential Minimum Energy Path (MEP) at the transition state and 
that associated with the reactant asymptote with \( k_B \) being the usual Boltzmann constant and \( T \) 
the temperature. The lowest approximation level formulates the pre-exponential factor as 
\( k_B T / h \) where \( h \) is the Plank constant.

In the adsorption of gaseous species, however, the most frequently used expression for the 
rate of reaction is the well known Hertz-Knudsen equation:
\[ r_{\text{ad}}^i = S_{0,i} \cdot A_{\text{site}} \frac{p_i}{\sqrt{2\pi m_i k_B T}} \] (2)

where \( S_{0,i} \) is the sticking coefficient (for which we take the value 1 in this work), \( A_{\text{site}} \) is the area of the adsorption site, \( p_i \) is the partial pressure of species \( i \) and \( m_i \) its mass.

A more accurate formulation of the rate coefficients makes use of the partition function for both, the intermediate state (incorporating so far the information about the remaining degrees of freedom) and the reactants:

\[ A = \left( \frac{k_B T}{h} \right) \left( \frac{Q^*}{Q_r} \right) \] (3)

where \( Q^* \) is the transition state partition function and \( Q_r \) the partition function of reactant species.

Each partition function is calculated considering that rotations and translations are frustrated (hindered), due to the fact that they are adsorbed, and therefore can be assimilated to vibrational degrees of freedom. In that case, the vibrational partition function takes the form:

\[ Q_{\text{vib},X} = \prod_k \frac{\exp \left( -\frac{h\nu_k}{2k_B T} \right)}{1 - \exp \left( -\frac{h\nu_k}{k_B T} \right)} \] (4)

where \( Q_{\text{vib},X} \) is the total vibrational partition function of the species \( X \), and \( \nu_k \) is the frequency of the vibrational mode \( k \).

In this way ZACROS can also simulate desorption/reaction spectra at a given temperature providing so far a rationale for designing kinetic mechanisms and understanding experimental data.
The elementary processes considered for the simulations are given in refs. [21,22] together with the numerical value of the related parameters. Hexagonal periodic default lattice will be the one of our choice for the Ziff, Gulari and Barshad (ZGB) reference model [23] as well as for the Sabatier Process.

An important outcome of our calculations is illustrated in Fig. 5 (see also ref. [19]) in which, in contrast with the suggestion of ref. [21] of a dominance of the CO\(^*\) decomposition, it is apparent from the analysis of the ZACROS calculations that the dominant process leading to the production of CH\(_4\) is the hydrogenation of CO. This has suggested us to investigate possible alternative gas phase processes producing CO. For this reason, we decided to investigate the possibility of inducing CO\(_2\) dissociation and producing CO\(^+\)O and CO\(^+\)+O\(^+\) neutral and ionic chemical pairs reacting with hydrogen, respectively, via a plasma generation either by electrical discharges or by vacuum ultraviolet (VUV) photons on a CO\(_2\)+H\(_2\) gas mixture as will be discussed in the next section.

4. Methane production from the CO\(_2\)+H\(_2\) reaction without solid phase catalysis

The investigations carried out on our ProGeo 20kW apparatus [22] based on the well-known Sabatier reaction:

\[
\text{CO}_2 + 4 \text{H}_2 \rightleftharpoons \text{CH}_4 + 2 \text{H}_2\text{O} \quad \Delta H_{298}^\circ = -165 \text{ kJ mol}^{-1}
\]  

at moderately high pressure (2-3 atm) and high temperature (200-300°C) with the use of a solid phase catalyst (nickel, ruthenium, or alumina) has prompted us to further progress (as will be illustrated in detail in this section) to use either low cost or renewable energy to reuse waste CO\(_2\) to produce methane in a circular economy scheme [22]. To this end we have undertaken the investigation of a new methanation pathway aimed at avoiding the use of the solid phase catalysis, by exploring mechanisms involving a plasma generation by electrical discharges or by vacuum ultraviolet (VUV) photons on a CO\(_2\)+H\(_2\) gas mixture. This effort is
based on the since long established expertise of our laboratories in promoting and modeling molecular processes (atomic hydrogen and excited metastable species generation by electrical discharge [24-26] to study gas phase processes induced under controlled conditions) and in fully characterizing the microscopic dynamics of elementary reactions by experimentally determining related main kinetic parameters such as rate constants, cross sections, intermolecular potentials, structure, and energy of the transition state, reaction pathways, etc. Furthermore, we can perform high resolution experiments in single collision conditions using crossed molecular beam apparatuses and studying plasma induced gas phase reactions both by microwave and RF (Radio Frequency) discharges [24-26] and by synchrotron radiation [27-29]. In particular the mentioned experiments are performed on the crossed molecular beams apparatus of the Perugia University [30,31] to measure PIES (Penning Ionization Electron Spectroscopy) data, and on the ARPES (Angle Resolved PhotoEmission Spectroscopy) end station at the GasPhase Beamline of the Elettra Synchrotron Radiation Facility (Trieste) [32,33] (more details are given later in the specific subsection).

The need of avoiding the use of the solid phase catalyst to perform reaction (5) and investigating possible alternative microscopic reaction mechanisms occurring in the homogeneous gas phase, is motivated by concurrency of reaction (5) and the following two main reactions:

\[
\begin{align*}
\text{CO} + 3 \text{H}_2 & \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O} \quad \Delta H_{298}^\circ = -206.1 \text{kJ mol}^{-1} \quad (6) \\
\text{CO} + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2 + \text{CO}_2 \quad \Delta H_{298}^\circ = +41 \text{kJ mol}^{-1} \quad (7)
\end{align*}
\]

as well as by the wish of avoiding unwanted reactions, like the (8), (9), (10), and (11) listed below,

\[
\begin{align*}
\text{CO}_2 + 2 \text{H}_2 & \rightleftharpoons \text{C} + 2 \text{H}_2\text{O} \quad \Delta H_{298}^\circ = -90.1 \text{kJ mol}^{-1} \quad (8) \\
2 \text{CO} & \rightleftharpoons \text{C} + \text{CO}_2 \quad \Delta H_{298}^\circ = -172.4 \text{kJ mol}^{-1} \quad (9) \\
\text{CO} + \text{H}_2 & \rightleftharpoons \text{C} + \text{H}_2\text{O} \quad \Delta H_{298}^\circ = -131.3 \text{kJ mol}^{-1} \quad (10)
\end{align*}
\]
\[ \text{CH}_4 \rightleftharpoons \text{C} + 2 \text{H}_2 \quad \Delta H_{298}^\circ = +74.8 \text{ kJ mol}^{-1} \]  

responsible for a rapid loss of catalytic activity. Further reservations on the use of a Ni based solid phase catalyst are related to the environmental and safety issues associated with the possible formation of Ni(CO)$_4$ that is a highly toxic gaseous species produced when Ni is exposed to a gas mixture containing high pressure CO as typical of experimental conditions commonly used to maximize the yield of CH\(_4\) in the methanation reaction.

For this purpose we have undertaken the study of the Sabatier reaction (5) in a homogeneous gas phase environment by generating and characterizing controlled plasmas via electrical discharges and VUV photons on a pure CO\(_2\) and CO\(_2\)+H\(_2\) gaseous mixture a technology in which our research group is leader since early 1990 [24,34,35]. In our experimental apparatuses (described in the next section) the energy pumped in the produced plasma can be controlled using both electrons and photons. In the first case we use an inhouse electrical microwave or RF discharge. In the second case we use a tunable synchrotron radiation. At the same time we can control and characterize the chemistry of the generated plasmas by studying the microscopic dynamics of the elementary chemical reactions because in molecular beam techniques [38-40] they occur in single collision regime (see again below in the specific subsection).

4.1. Experimental methods

As already mentioned, a first attempt to produce plasmas containing carbon dioxide, has been made in our laboratory using a microwave discharge beam source operating in pure CO\(_2\) and in an approximately 50-50\% CO\(_2\)-H\(_2\) mixture at a global pressure of about 1600 Pa. The microwave discharge is produced in a cylindrical quartz tube (10 cm in length and 2 cm in diameter) in a brass resonance cavity (water cooled) working at 2450 MHz [24,34,35]. The applied microwave power was varied in the range 70-200 W with a reflected power lower
than 5%. A preliminary characterization of the produced plasma has been performed using the crossed molecular beam apparatus shown in Figure 6. Such an apparatus, usually devoted to the study of the microscopic dynamics of autoionization reactions induced by excited metastable species (also called Penning Ionization or Chemi-ionization reactions), for the experiment considered here was used by keeping the secondary beam switched off. In this way it was possible to detect only the main chemical species flowing out of the plasma microwave discharge source as an effusive molecular beam. Such an analysis was performed using the mass spectrometry characterization of the beam by means of a quadrupole mass filter located below the crossing beams region. Measured data is consistent with that previously recorded by Dobrea et al. [39,40] who found a large dissociation rate of carbon dioxide, according to reactions (12) and (13) below, in the case of the plasma discharge in pure CO$_2$ with respect to the one measured in CO$_2$+H$_2$ gas mixture.

\[
\text{CO}_2 + e^- \rightarrow \text{CO} + \text{O} \quad (12)
\]

\[
\text{O} + \text{O} \rightarrow \text{O}_2 \quad (13)
\]

The CO$_2$ dissociation percentage, \( \chi \) (determined by keeping the inlet gas pressure at a constant value of 1600 Pa) was obtained by recording the CO$_2^+$ intensities \( I_i \) and \( I_f \) (measured with the microwave discharge off and on, respectively) using the following relationship:

\[
\chi = \frac{I_i - I_f}{I_i} \cdot 100 \quad (14)
\]

The values of \( \chi \) amounted to about 27% in the case of the plasma discharge in pure CO$_2$, and lowered to about 19% in the case of CO$_2$+H$_2$ gas mixture at an applied microwave power of 100 W. The measured values increased up to 52% (for plasma in pure CO$_2$) and 36% (in plasma in CO$_2$+H$_2$ mixture) when the microwave power was doubled to about 200 W. Measured data is reported in Table 1 and compared with that of refs. [39,40]. Then the same apparatus of Figure 6 was used to measure plasma-assisted CO$_2$ conversion into hydrocarbons as an alternative way of producing synthetic fuel (this technique has been
recently applied by Welzel et al. [41] who determined the experimental conditions suited to give a 20% yield for CH$_4$ formation. We better characterized the chemistry of the produced plasmas by investigating the detail of the chemical reactions induced by the ionic species that can be formed in such gaseous environments using VUV photons as a source of energy to induce excitation and ionization processes responsible for the plasma generation. The experiment was performed at the ELETTRA Synchrotron Light Laboratory (Trieste, Italy), using the ARPES end station at the Gas Phase having a very high photon intensity and a tunable wavelength. Details of the beam-line and of the end station have been already reported elsewhere [42,43] and the characteristics of the apparatus used for the experiment are discussed in detail in refs. [44,45]. Specific features of the experiment reported here are: i) the use of a synchrotron radiation tunable energy source, working in the energy range of 35-50 eV with a resolution of about 1.5 meV; ii) the detection of all produced charged particles (electrons and ions) in the generated plasma, recording them in a time resolved measurements in which we are able to extract the spatial momentum components of final ions by using the electron-ion-ion coincidence technique coupled with an ion position sensitive detector (see below).

Figure 7 shows: i) on the left hand side panel, a scheme of the main part of the experimental apparatus based on the electron-ion-ion coincidence technique, and, as an example, the coincidence plot recorded in the double photoionization experiment of carbon dioxide at a photon energy of 44 eV (in such a panel are also shown the recorded mass spectra of the product ions at the same photon energy); ii) on the right hand side panel, a picture of such a device. As can be seen from the Figure, the monochromatic synchrotron light beam crosses at right angles an effusive molecular beam of CO$_2$ neutral precursors, and the product ions are then detected in coincidence with photoelectrons. The coincidence electron-ion-ion extraction and detection system consists in a time of flight (TOF) mass spectrometer equipped with an
ion position sensitive detector (stack of three micro-channel-plates with a multi-anode array arranged in 32 rows and 32 columns). As mentioned above, such a detector has been especially designed in order to properly measure the spatial momentum components of the ionic products [46].

Carbon dioxide was supplied from a commercial cylinder at room temperature (99.99% nominal purity) to a needle effusive beam source. An adjustable leak valve along the input gas pipe line was used in order to control the gas flow, which was monitored by checking the pressure in the main vacuum chamber.

4.2. The chemical role of CO$_2$ in the generated plasma

When using excitation energies higher than 35 eV, it is possible to induce ionization phenomena in gaseous mixtures containing carbon dioxide with the production of CO$^+$, O$^+$ and CO$_2^{2+}$ ions (as a matter of fact plasmas constitute over 99% of the known matter of the Universe). Indeed, the formation of doubly charged positive ions in gas phase using VUV photons or energetic electrons as ionizing source is routine in a number of laboratory experiments able to reproduce the physical conditions of the upper atmosphere of some planets of the Solar System (such as Mars, Venus, and Titan) [27-29, 49-52]. Once these ionic species are produced in metastable states, after their typical lifetime they can, dissociate into ionic fragments having a high kinetic energy content due to the strong Coulomb repulsion characterizing the low stability of their electronic structure. This so called “Coulomb explosion” of molecular dications provides their fragments with a large amount of translation energy (several eV) that enhances the chemical reactivity of the plasma with the following consequences on the properties of a gas mixtures: i) the chemical behavior is radically changed because the removed electrons may change sensibly the electronic configuration of the neutral species and modify its chemical reactivity; ii) the interaction is much more intense
than the neutral-neutral one, making more likely collision events and increasing the chemical reactivity in plasma environments; iii), the formation of fragment ions with large kinetic energy increase chemical reactivity.

In particular our experiments with a plasma containing $\text{CO}_2$ confirmed the carbon dioxide dissociation paths singled out by previous studies [53-56] and quantified the following ones allowed to indicates that the following main processes are possible with their respective threshold energies:

\[
\begin{align*}
\text{CO}_2 + h\nu &\rightarrow (\text{CO}_2^+) + e^- \rightarrow \text{CO}^+ + O^+ + e^- \rightarrow \text{CO}^+ + O^+ + 2e^- & h\nu \geq 35.6 \text{ eV} & (15) \\
\rightarrow \text{CO}_2^{2+} + 2e^- & & h\nu \geq 37.3 \text{ eV} & (16) \\
\rightarrow (\text{CO}_2^{2+})_{\text{long lived}} + 2e^- & \rightarrow \text{CO}^+ + O^+ + 2e^- & h\nu \geq 38.7 \text{ eV} & (17)
\end{align*}
\]

Figure 8 shows the relative cross sections measured in the investigated photon energy range for reactions (15), (16), and (17) recorded using the electron-ion-ion coincidence technique discussed in the previous section. The analysis of data, collected at each investigated photon energy, is based on the density distribution evaluation of coincidences in the measured coincidence spectra, such as the one reported in the left panel of Fig. 7. On such an analysis, the total counts (recorded at each investigated photon energy) corresponding to the ion pair peak coming out from the same reaction gives the relative cross section for the three investigated reaction channels of Fig. 8. At the same time, the KER (Kinetic Energy...
Released) of product ions can be evaluated by analyzing the dimension and the shape of the recorded peaks using the method suggested by Lundqvist et al. [57]. This procedure, applied to the CO²⁺/O⁺ coincidences signal related to reactions (15), (16) and (17), has allowed us to evaluate the KER distributions of all product ions for different values of the investigated photon energy (36.0, 39.0, 41.0, 44.0 and 49.0 eV). The results shown in Fig. 9 tell us that the KER value for the O⁺ ions ranges between 1.0 and 5.0 eV, while the CO⁺ KER can reach 3.0 eV or more and, changes the maximum value depending on the investigated photon energies. These results demonstrate that the chemical reactivity of plasmas containing CO₂ is strongly increased by the presence of CO⁺ and O⁺ ions having a very high kinetic energy. In particular, the fast CO⁺ ions, are expected to react with molecular and atomic hydrogen (both produced in a plasma generated by a microwave discharge in a gaseous CO₂+H₂ mixture [24-26, 39,40]) playing a pivotal role in the plasma-assisted CO₂ conversion on CH₄ fuel. In this respect, it has to be noted that Knott et al. measured reactive cross section for the CO⁺+H₂→HCO⁺+H reaction, obtaining a related rate constant value ranging between 1.6 x10⁻⁹ and 3.0x10⁻⁹ cm³ s⁻¹ in the collision energy range of 0.01 – 3.0 eV, indicating a pronounced decline at elevated collision energies, higher than 7.0 eV [58]. An analogous situation has been recorded by Farrar and coworkers in their study of H₂⁺+CO proton transfer reaction producing HCO⁺ in the 0.74 - 9.25 eV collision energy range [59]: at higher energies, the cross section drops rapidly whereas, at low energies, the HCO⁺ products are highly excited, with 90% of the available energy in internal excitation.

A first consideration can be made regarding the production of a low energy CO₂-H₂ plasma. In such a case, it has to be noted that, by using CO⁺ ions coming from the Coulomb explosion of CO₂²⁺ molecular dication, a projectile reactive species is available with a translational energy content of about 2.0-2.5 eV (see Fig.9). This means that in our plasma the CO⁺+H₂ reaction, also favored by a stronger long range trapping attraction, can occur with a
rate constant value higher than those of neutral-neutral reactions (having in most cases typical
rate constant values of about $10^{10}$-$10^{12}$ cm$^3$ s$^{-1}$ [60]). In the case of the production of high
energy CO$_2$-H$_2$ plasmas, further considerations can be made, in order to take into account that
the CO$^+$+H$_2$ measured cross section shows a strong decrease when the collision energy
becomes higher than 7 eV [58]. In this case, Knott et al. explain their results by invoking a
dissociation process of the HCO$^+$ product with a threshold beyond 7.0 eV. In fact, since CO$^+$
($\overset{3}{\Sigma}$ symmetry) has a predissociating state close to 8.0 eV (vertical) [61] and the vertical
transition to the first excited state of H$_2$ ($\overset{3}{\Sigma}_u^+$) represents a step of about 9.0 eV, the CO$^+$+H$_2$
collision should result in an excitation of CO$^+$ rather than of H$_2$. We fully agree with such
authors and it is important to note that the possible predissociation of CO$^+$ appears to be
energetically accessible at lower energies (about 5 eV) as demonstrated by more recent
calculations by Okada and Iwata [62]. Furthermore, Nobes and Radom in 1981 [63] first
calculated the energy profile for the fast isomerization reaction between HCO$^+$ and COH$^+$
demonstrating a higher stability for HCO$^+$ and a triangular structure of the [HCO]$^+$
intermediate complex. This corroborates the absence of H$_2^+$+CO and CO+H$^+$+H possible
competitive products in the CO$^+$+H$_2$ reaction for which Knott et al. [58] have recorded only
HCO$^+$ ions with any evidence of both H$_2^+$ and H$^+$ products. In their analysis such authors,
following ref. [61], did not consider the possibility of the HCO$^+$ with the rupture of the C---O
bond, because their relatively low investigated collision energy range. Moreover, such a
dissociation process is energetically allowed and can occur in high energy CO$_2$-H$_2$ plasmas,
where the formed HCO$^+$ ions are compatible with electron attachment dissociation processes
towards the production of CH+O neutral reactive species, as demonstrated since 1972 by
McGregor and Berry [64].

Finally, the efficient conversion of CO$^+$ and CO$_2^+$ ions into HCO$^+$ by collisions with
H$_2$ and H reactive partners (all these species can be formed in a CO$_2$-H$_2$ plasma), with the
HOC$^+\leftrightarrow$COH$^+$ isomerization, has been experimentally observed by Gerlich and coworkers [65, 66] and by Tosi et al. [67], corroborating the observation that in plasma environments HCO$^+$ results a very stable species as it is confirmed by astronomical observations indicating HCO$^+$ as one of the most important ions in dense molecular clouds [68,69].

In conclusion, it appears that the production of a CO$_2$-H$_2$ plasma by a microwave discharge allowed us to generate: i) a large dissociation of carbon dioxide, according to reactions (12) and (13) (see data of Table 1); and ii) CO$_2^+$, CO$_2^{2+}$, CO$^+$ and O$^+$ ionic species (see reactions (15)-(17) and Figures 8 and 9) able to react with atomic and molecular hydrogen in order to produce HCO$^+$ ions. All such experimental evidences are compatible with the possible formation of CH and CH$^+$ species, being the first hydrogenation step on the carbon atom, for a plasma-assisted CO$_2$ conversion into hydrocarbons as an alternative transformation route in synthetic fuel processing.

Further experimental work is in progress in our laboratory in order to investigate such possibility, and to optimize the experimental conditions in an attempt to perform the CO$_2$ hydrogenation reaction (5) via an alternative microscopic mechanism with respect to the use of the solid catalyst.

5. Conclusions

The reported concerted efforts of University, ENEA and SMEs researchers in investigating engineering and distributed computing have shown in this paper to what extent the advances in basic research on plasmas are amenable to the assembling of an experimental prototype applying the Sabatier reaction to a homogenous gas phase catalytic environment and to the activation of a circular process turning waste CO$_2$ flue gases into methane. The measurements performed have not only shown the viability of the proposed solution but have also allowed the extension of computer simulations to a family of innovative mechanisms.
Furthermore, as a result of the investigation, useful indications have been obtained on how to proceed to develop alternative solutions to the present Ni catalysed Progeo apparatus by resorting to a gas-phase-only process for the reduction of CO$_2$ to CH$_4$. In this work new results obtained by electrical discharges into CO$_2$-H$_2$ gas mixtures by using molecular beam technique at different pressure regimes has been presented. Such results together with VUV CO$_2$ photoionization data collected by synchrotron radiation are then of great help in identifying the microscopic mechanisms to be exploited. Finally, the production of a CO$_2$-H$_2$ plasma by a microwave discharge allowed us to generate a large dissociation of carbon dioxide, and to produce CO$_2^+$, CO$_2^{2+}$, CO$^+$ and O$^+$ ionic species able to react with atomic and molecular hydrogen in order to produce HCO$^+$ ions. All such experimental evidences are compatible with the possible formation of CH and CH$^+$ species, representing the first hydrogenation step on the carbon atom, for a plasma-assisted CO$_2$ conversion into hydrocarbons. This is an alternative transformation route in synthetic fuel processing that we shall investigate further to the end of grounding Progeo on more robust methanation processes.

Acknowledgements

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Table 1 – The percentage of CO$_2$ dissociation in microwave discharge plasma source produced in pure CO$_2$ and in a 1:1 CO$_2$/H$_2$ gaseous mixture for different values of applied microwave power. The percentage values are calculated using the simple equation (2), and are collected working at a constant pressure of 1600 Pa into the plasma source (see text). The data are compared with those previously collected by Dobrea et al. in an analogous experiment performed at a constant pressure of about 600 Pa [41,42].

<table>
<thead>
<tr>
<th>Microwave discharge power (W)</th>
<th>% of CO$_2$ dissociation in pure CO$_2$ plasma</th>
<th>% of CO$_2$ dissociation in a 1:1 CO$_2$/H$_2$ plasma mixture</th>
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<tbody>
<tr>
<td></td>
<td>This work</td>
<td>ref. [14]</td>
</tr>
<tr>
<td>70</td>
<td>19±4</td>
<td>---</td>
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<tr>
<td>100</td>
<td>27±3</td>
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<tr>
<td>200</td>
<td>51±2</td>
<td>48</td>
</tr>
</tbody>
</table>
Figure captions

Fig. 1. 2500X micrography of the commercial catalyst KATALCO\textsubscript{JM} 11-4MR (by courtesy of University of Rome Tor Vergata, Rome, Italy).

Fig. 2. A picture of the twin columns of the ProGeo reactor.

Fig. 3. Cross section of the reactor twin columns and locations of the related thermocouples (red dots). On the right hand side the labels of the thermocouples.

Fig. 4. Average measured percentage of the methane produced in our experiments plotted as a function of the molar ratio and of the temperature with a pressure of 2 bar.

Fig. 5. Relative contributions of the different elementary channels to the production of methane evaluated from the minimum energy path of the PES (triangle) and from the ZACROS simulation (diamonds, squares, reverse triangles for the different temperatures connected by solid lines). The green triangle is the value suggested in ref.\textsuperscript{[24]}.

Fig. 6. The crossed molecular beam apparatus (mainly used in Penning ionization studies and adapted for plasmas generation containing carbon dioxide) in which the secondary beam was maintained off in order to detect the main chemical species coming out as an effusive molecular beam from the plasma microwave discharge source (see text).
**Fig. 7.** The electron-ion extraction and detection system used for the electron-ion-ion coincidence measurements to characterize the charged species produced in the CO\(_2\) plasma by tunable synchrotron radiation. Left panel: a scheme of the set-up with a typical coincidence spectrum recorded by the double photoionization of CO\(_2\) at a photon energy of 44 eV (see text). Right panel: a picture of such a device.

**Fig. 8.** Measured cross sections for the three main processes observed in the CO\(_2\) plasma generation by using synchrotron radiation in the energy range of 34-50 eV and the electron-ion-ion coincidence technique (see text).

**Fig. 9.** Kinetic energy distributions for CO\(^+\) and O\(^+\) fragment ions originating by Coulomb explosion of CO\(_2^{2+}\) dication produced in the CO\(_2\) plasma by tunable synchrotron radiation.
Methanation Reactor: inner thermocouples in channels A and B

FIG. 3

FIG. 4
FIG. 5

% of CH₄ produced by channel

- CO decomposition
- C(OH)₂ formation
- CO hydrogenation
- CO disproportionation

Channel

Temperature:
- 700°C
- 900°C
- 1100°C

Legend:
FIG. 6

FIG. 7
$h\nu = 44\ eV$

- CO$_2$ effusive molecular beam source
- Crossing with synchrotron VUV beam
- Ions
- Electron MCP detector
- Ion optics
- Ion position sensitive detector
- Ion t.o.f. tube
FIG. 8

Stable molecular dication formation
$\text{equation (15)}$

Slow dissociation through long lived
dication metastable states
$\text{equation (16)}$

Fast molecular fragmentation
$\text{equation (14)}$
CO$_2$ + hv (or energetic electrons) → CO$_2^{2+}$ + 2e$^-$

![Graph with peaks at kinetic energies of 49, 44, 41, 39, and 36 eV.]