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Theses of the Ph.D. Dissertation

titled as

***Theoretical Study on Molecular Networks
of Carbon Dioxide to Methanol Conversion***

Presented

by

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Introduction

During the recently passed industrial phase of global civilization, energy production was mainly based on combustion. Sooner or later, this type of energy production will be replaced by alternative technologies, but until then, we must get through a transition period in the near future, during which the world has to focus on global CO₂ management.

According to the BP Statistical Review of World Energy 2019¹, the increase in the world's population is reflected in an increasing demand of energy within the economic sectors. Consequently, the annual consumption of primary energy is constantly increasing, thus causing an increased carbon dioxide emission in the atmosphere, which is one of the main contributors to global warming.

The proposed solutions are mainly Carbon Capture and Storage (CCS) methods², which do not definitively solve to this issue by eradicating the excess of CO₂ from the atmosphere³. Research in the energy sector led to what is called an “Energetic Transition”, which is the progressive replacement of fossil fuels (oil, natural gas, coal) by renewable energies (solar energy, wind energy, water energy, biomass). However, turning to renewable energies will require another problem to be solved, which is to find an effective energy storage method. We believe that CO₂ valorization, by chemically converting this molecule to other added-value molecules⁴ such as methanol⁵, is the one of the best ways to eliminate it, and this is called Carbon Capture and Usage (CCU)⁶. The CO₂ would be captured and hydrogenated⁷, and its product will be used in other useful processes, or even in combustion. The hydrogen can be generated by water electrolysis using renewable energies⁸.

Methanol is one of the most attractive added-value products of CO₂ reduction due to its high energy density, and it is an excellent precursor for the chemical industry⁹. In recent decades, CO₂ hydrogenation to methanol has been a widespread subject of interest, and large variety of solid catalysts have been designed and tested¹⁰. Nevertheless, the reduction mechanism is still a debated subject and new processes are continually being proposed¹¹.

Goal

The chemical hydrogenation of CO₂ to methanol by using renewable energies can be the key to solve the problem of renewable energy storage as well as to reduce CO₂ emissions.

However, carbon dioxide hydrogenation is a mechanistically complicated multi-step process. Therefore, it is indispensable to understand the mechanism. Computational chemistry tools can be used further to understand this process.

This thesis is an assembly of three major computational chemistry studies:

- A gas phase study: where all the molecular complexes that might be formed from the (CO₂+4H₂) reaction mixture are investigated and the most stable ones will be selected to be part of a newly designed network for the uncatalyzed carbon dioxide hydrogenation to methanol and methane. The energetics of the elementary steps constituting the network will be studied, and the efficiency of the most favourable pathway will be calculated.
- An aqueous phase study: knowing that carbon dioxide can be absorbed by water as it happens in the oceans, an uncatalyzed water enhanced hydrogenation mechanism for CO₂ conversion to methanol will be designed and thermodynamically studied. The efficiency of the preferred pathway will be calculated and compared to the gas phase results.
- An aqueous phase catalyzed-like study: the major role of a solid catalyst in the methanol synthesis is the conversion of hydrogen molecules to hydrogen atoms (bond dissociation). To mimic this property of the catalysts, a catalyzed-like mechanism will be constructed involving hydrogen atoms instead of hydrogen molecules and studied energetically. Thereafter the efficiency will be calculated taking into account the hydrogen bond dissociation energy.

These studies aim to provide a better understanding of this difficult process, and to identify and propose mechanisms to reduce the barrier height of the rate-limiting steps under different chemical conditions that can be directly applied to industrial settings. The findings can be applied in the near future to the design and development of new special-purpose catalysts for the 'elimination' of CO₂ and to reduce its detrimental effects on our global ecosystem.

Computational methods

For the identification of the most favourable mechanism with its elementary reaction steps in gas phase, combinatorial chemistry¹² software (MOLGEN 5.0¹³) in combination with *ab initio* calculations have been used. All possible molecular complexes that can form from the reactants mixture (CO_2+4H_2) were generated and optimized applying the B3LYP density functional theory (DFT) method^{14,15} in combination with the 6-31G(d) basis set¹⁶. The most stable structures were selected to construct a network for the hydrogenation of CO_2 to methanol and methane. The designed network was studied thermodynamically using the W1BD protocol¹⁷.

The hydrogenation of CO_2 to methanol was also studied in aqueous phase. Two molecular networks were designed. The first was a water enhanced mechanism involving a water molecule in the reaction steps, and the second one was designed to mimic the role of a heterogeneous catalyst by involving a hydrogen atom instead of a hydrogen molecule.

Both mechanisms were investigated energetically using computational chemistry methods. The B3LYP density functional theory (DFT) method^{14,15} in combination with the 6-31G(d) basis set¹⁶ was used as a first approach for the localization of the minimas and transition state energies, and then the unrestricted version of the (Weizmann-1) protocol was used to obtain more accurate results (W1U)¹⁸. Internal Reaction Coordinates (IRC)¹⁹ calculations have been used to verify if the transition states are located between the corresponding minima. To compute the reactions in the aqueous phase, the solvent effect on the reaction was taken in account by using the SCRF implicit solvation model²⁰. All calculations were carried out using the Gaussian 09 program package²¹.

To estimate the accuracy of the computational method, the heat of formation of 10 optimized structures have been calculated using the W1 composite method and have been compared to highly accurate experimental values from the literature. The average deviation observed from the experimental results was **0.985 kJ/mol**.

New scientific results

1st Thesis

Several uncatalyzed reaction routes of CO₂ to methanol conversion have been designed and studied in gas phase where 9 intermediate molecular complexes were involved. The thermochemical properties have been computed and the overall potential energy surfaces (PES) have been drawn.

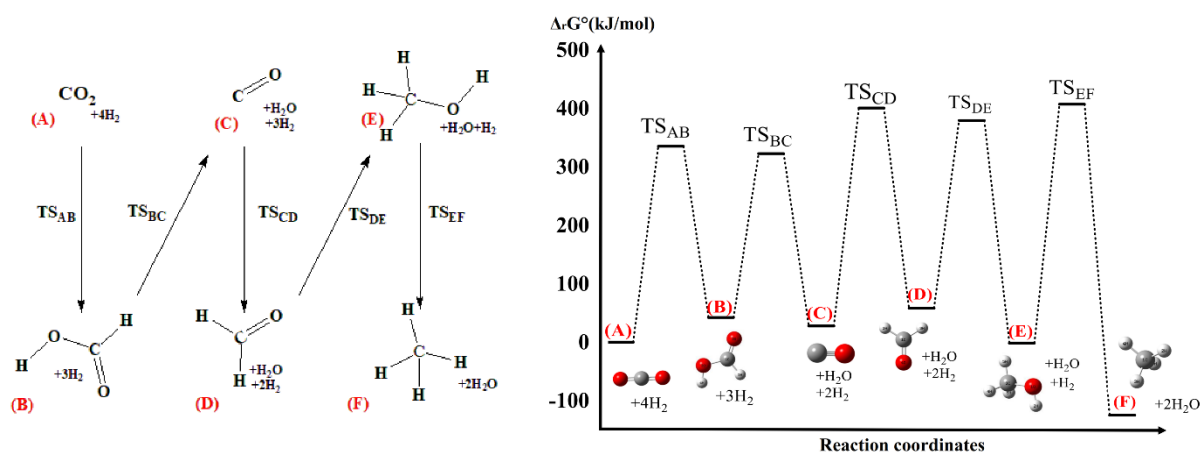


Figure 1: Preferred mechanism pathway of the uncatalyzed CO₂ conversion to methanol and methane in gas phase and its corresponding potential energy surface.

Among the several possible pathways, the most favourable ones have been selected and discussed (**Figure 1**, left). The corresponding PES is shown in (**Figure 1**, right). We have shown that the uncatalyzed gas phase CO₂ hydrogenation is thermodynamically unavailable considering its rate determining step $\Delta G_{(\text{Gas})} = 400.66$ kJ/mol.

2nd Thesis

In the newly designed uncatalyzed aqueous phase CO₂ reduction mechanism (**Figure 2**). The energy barriers are significantly lower than in the gas phase (about 100 kJ/mol lower). The most favorable route has been found within the aqueous phase catalyzed-like hydrogenation mechanism (**Figure 2**).

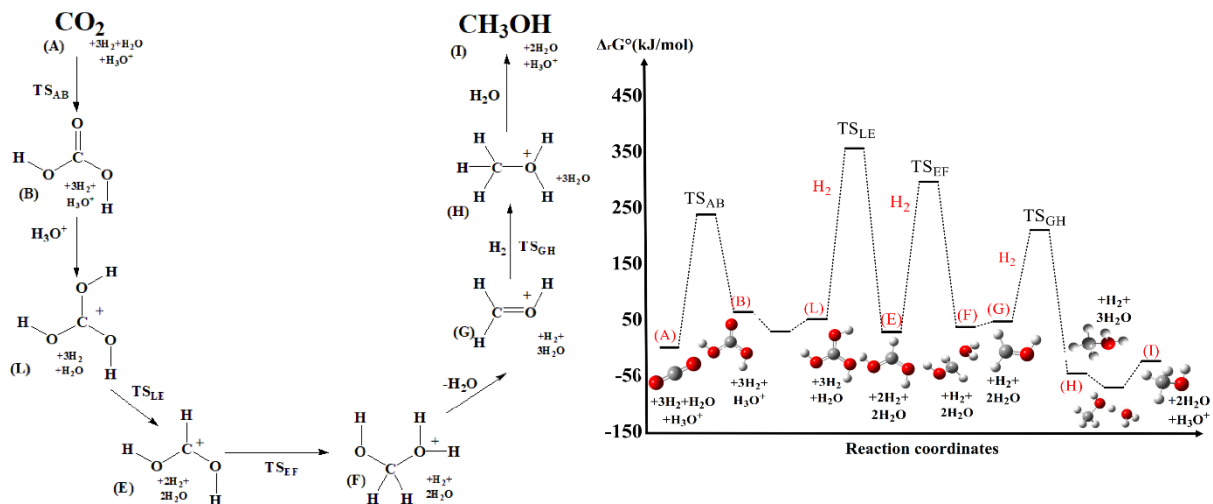


Figure 2: Preferred mechanism pathway of the water enhanced mechanism of CO₂ conversion to methanol and its corresponding potential energy surface.

There is only one barrier above 300 kJ/mol in the uncatalyzed version of the aqueous phase mechanism ($\Delta G_{\text{(Aqueous)}} = 355.52$ kJ/mol).

3rd Thesis

Further improvement and a significant decrease of the energy barriers was observed in the catalyzed-like mechanism (**Figure 3**), where the highest barrier is only equal to $\Delta G_{\text{(H)}} = 212.67$ kJ/mol.

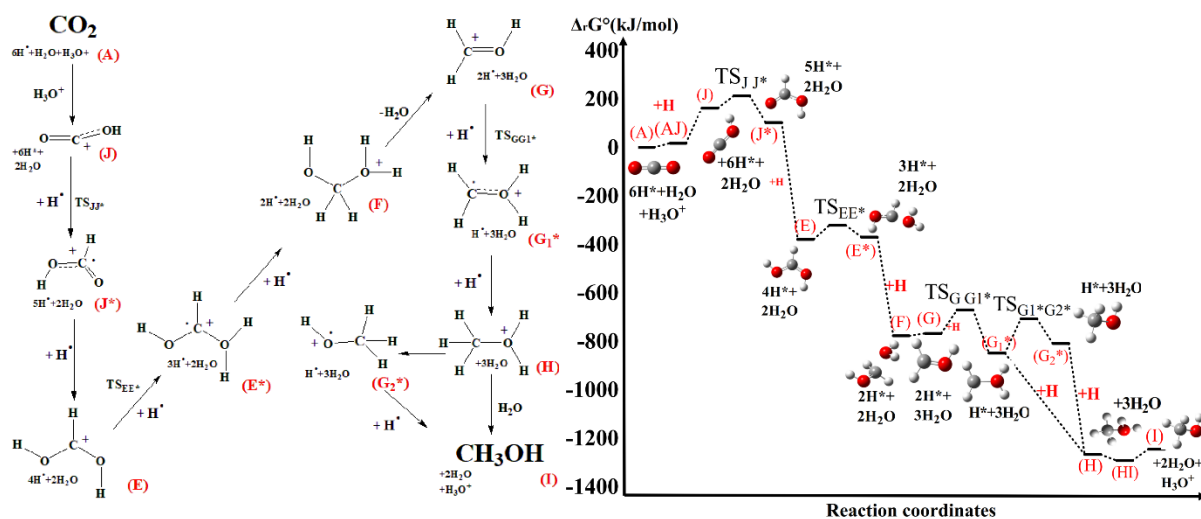


Figure 3: Preferred mechanism pathway of the catalyzed-like water enhanced mechanism of CO₂ conversion to methanol and its corresponding potential energy surface.

Based on the energetics of the studied mechanisms and the calculated efficiencies, it can be concluded that the atomic hydrogenation mechanism is a key process for CO₂ reduction,

because of its relatively low energy barriers and high efficiency ($\eta_{(H\cdot)} = 92.5 \%$). This mechanism can be achieved by using appropriately selected/designed catalysts or electrocatalytic systems.

4th Thesis

We have introduced the concept of energy storage efficiency. This allows us to compare the most favourable pathways of the conversion of CO₂ to methanol in each case. The aqueous phase processes have a better efficiency over the gas phase mechanism. The efficiency is almost doubled in the non-catalyzed case: $\eta_{(Aqueous)} = 27.1\%$ vs $\eta_{(Gas)} = 14.4\%$. Mimicking the catalytic process in aqueous phase leads to an enormous increase and it is 3.4 times more efficient than the gas phase non-catalyzed process ($\eta_{(H^*)} = 92.5 \%$).

5th Thesis

The W1 composite method has been selected for all calculations and its applicability to describe the thermochemistry of the studied processes (and other similar reactions) has been verified. The method has been tested and compared to experimental values. The average deviation observed from the experimental results is equal to **1.61 kJ/mol = 0.39 kcal/mol**.

Summary

The high capacity storage of the renewable electrical energy can be completed with the Substitute Natural Gas (SNG) alternative. The SNG alternative is the chemical bounding of hydrogen obtained from electrolysis using renewable electricity and the carbon dioxide which can be obtained from several sources. This will for sure contribute to the reduction of the emissions of it in the atmosphere. However, the conversion of CO₂ to methanol is a rather complicated multistep process. The reduction of carbon dioxide has several reaction steps and intermediate products. Newly developed uncatalyzed and catalyzed-like mechanisms have been envisaged and studied thermodynamically in gas phase and aqueous phase using computational chemistry tools. The Gibbs free energy change of the preferred pathways of the uncatalyzed and catalyzed-like mechanisms have been described (**Figure 1, 2, and 3**).

By comparing the uncatalyzed gas phase and aqueous phase processes the following conclusions can be drawn:

- In both cases, the highest energy barriers are hydrogenations.
- The highest energy barriers in the preferred pathways of the two mechanisms are equal to $\Delta G_{(\text{Gas})} = 400.66 \text{ kJ/mol}$ and $\Delta G_{(\text{Aqueous})} = 355.52 \text{ kJ/mol}$.
- Considering the efficiencies of these mechanisms, the aqueous phase mechanism is almost two times more efficient than the gas phase ($\eta_{(\text{Aqueous})} = 27.1\%$ vs $\eta_{(\text{Gas})} = 14.4\%$).
- We notice that in the gas phase mechanism (**Figure 1**) the reaction barriers are the highest between the three PESs. In the preferred pathway of the aqueous phase mechanism (**Figure 2**) the energy barriers are already lower.
- The efficiencies can be increased by decreasing the energy barriers (hydrogenations). This can be achieved by involving hydrogen atoms instead of hydrogen molecules, which can be realized by using a catalyst or an electrocatalytic systems.
- Since the uncatalyzed aqueous phase mechanism has a better efficiency it was used as a starting point. Hydrogen molecules have been replaced by hydrogen atoms and a catalyzed-like mechanism have been designed (**Figure 3**).
- After analyzing the catalyzed-like mechanism, further improvement and a significant decrease of the energy barriers was observed in the overall process and the corresponding energy barriers are significantly lowered. In the preferred pathway, the

highest barrier is only equal to $\Delta G_{(H^*)} = 212.67$ kJ/mol which compared to the uncatalyzed mechanism, is almost twice smaller. Thus, a considerable increase has been achieved in the efficiency. The catalyzed-like mechanism is 3.4 times more efficient than the gas phase non-catalyzed process ($\eta_{(H^*)} = 92.5\%$).

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Publications

Publication bibliometrics

Number of papers published:	2
Number of papers under review:	1
Cumulative impact factor related to the thesis:	9.275
Total number of citations:	4

Scientific publications

1. R. Hadjadj, Rachid Hadjadj, Csaba Deák, Árpád Bence Palotás, Péter Mizsey, Béla Viskolcz, Renewable energy and raw materials – The thermodynamic support, *Journal of Cleaner Production*, doi:10.1016/j.jclepro.2019.118221. (Q1; IF = 7.246)
2. R. Hadjadj, Imre G.Csizmadia, Péter Mizsey, Svend Knak Jensen, Béla Viskolcz, Béla Fiser, Water enhanced mechanism for CO₂ – Methanol conversion, *Chemical Physics Letters*, doi:10.1016/j.cplett.2020.137298. (Q2; IF = 2.029)
3. Catalysed-like mechanism for CO₂ conversion to methanol, *Arabian journal of chemistry*, under review, 2020.

Oral and Poster presentations

1. 9th Visegrad Symposium on Structural Systems Biology, Water catalysed reduction of CO₂ to methanol in Aqueous-phase, Szilvásvárad, Hungary, 2019, *Poster*.
2. 1st Science Unlimited Conference – Eötvös Symposium, Uncatalyzed molecular network for CO₂ hydrogenation to methanol and methane, Miskolc, Hungary 2019, *Oral presentation*.
3. 25th International Symposium on Gas Kinetics and Related Phenomena, Detailed molecular network of CO₂ hydrogenation 2018, Lille, France, *Poster*.
4. Conversion of CO₂ to CH₃OH - A mechanistic study, XXIII. Bolyai Conference, 2018, Budapest, Hungary, *Poster*.
5. 7th Visegrad Symposium on Structural Systems Biology, Systematic theoretical investigation for high energy C₂H₈O₄ molecules, Nove Hradky, Czech Republic, 2017, *Poster*.

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