A numerical study of plasma-catalytic dry reforming

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> **Abstract:** This work aims to study on a theoretical point of view the pulsed powered plasmacatalytic dry reforming by using a chemical kinetics model which includes at the same time homogeneous chemistry and heterogeneous one. Thus, by considering the main gas-phase and surface reactions involving in plasma-catalytic dry reforming, zero-dimension numerical simulations have been done to investigate the separate roles of plasma and heterogeneous catalysis according to the operating conditions and thus to calculate the reaction barriers.

Keywords: Plasma-catalysis, Dry reforming, Kinetics, Activation energy.

1.Introduction

Carbon dioxide and methane, two greenhouse gases (GHGs), play an undeniable role in the current global warming. Catalytic transformation of CO_2 to valuable chemicals may help to reduce the CO_2 emission in the atmosphere as well as to create a sustainable low carbon economy. Plasma activation of a CO_2/CH_4 mixture under strong electric fields creates high rates of reactive species (ions, excited species, radicals) in the gas phase in ambient physical conditions. Coupled to the heterogeneous catalysis, a new promising route for dry reforming can thus be drawn. Many researches (experimental and theoretical) have been devoted to the development of high-efficient plasma-catalytic conversion of greenhouse gases to valuable chemicals for the last decade and most of them are meaningful and promising [1].

In parallel to experimental studies, numerical modelling provides a powerful approach to describe the insight of the plasma from a theoretical point of view [2-4]. It helps to describe the physicochemical phenomena of the process and predict the behaviour of the plasma. Unfortunately, to our best knowledge, few of them involved the catalysts and surface mechanism while it is critical in the real process. Hence, in this new pioneer work focus on that by integrating the plasma chemistry and surface reactions on the catalysts at the molecular level which contribute to establish a more comprehensive reaction networks of micro-kinetics in plasma catalysis. Apart from analysing the number density of reactants, products and intermediates, we also calculated the activation energy, an essential kinetic parameter, to demonstrate the role of catalysts in plasma process.

2. Methods

0D kinetic model ignores the configuration of plasma reactor and the effects of catalysts (as shown in Fig. 1). For a general elementary reaction in proposed mechanism:

$$A_m + B_m \leftrightarrow C_m + D_m \tag{1}$$

According to the method presented in the literature, [5] energy barrier (E_a , kJ mol⁻¹) of the NTP-catalysis was obtained by using a modified Arrhenius law:

$$r_i = A_i \times e^{\frac{F * Ea_i}{P_p}}$$
(2)

Where i can be p (for plasma alone) or pc (for plasmacatalysis), thus, rp is the reaction rate of plasma-assisted dry reforming without catalysts, r_{pc} is the reaction rate of plasma-assisted dry reforming over catalysts, F is the total flow rate of feed gas (50 mL min⁻¹), while P_p is the plasma power (W). In this work, the conversion rate of CO_2 and CH₄ are calculated by using a plasma Perfectly Stirred Reactor (PSR) reactor and the DBD discharge power is fixed between 2 and 3 W. The activation energy of plasmacatalytic dry reforming was also obtained by using a modified Arrhenius law. Now, what we aimed to see were the differences between A_p and A_{pc} from one side, and Ea_p and Eapc from another side. Ap and Eap represent Arrhenius rate coefficients and activation energy for plasma alone process respectively, while Apc and Eapc represent those in plasma-catalysis. For both plasma-catalysis, ln (r_i) and the inverse of plasma power $(1/P_p)$ are plotted, then the slopes are obtained by linear fitting of them according to:

$$\ln(r_i) = Ea_i \times F \times \frac{1}{P_p} + \ln(A_i)$$
(3)



Fig. 1. Diagram of modelling.

3. Discussion

We apply one plasma pulse which is simplified based on the voltage and current measured from our plasma reactor. In our modelling, the power is input during a pulse duration of 60 ns then stopped during an afterglow period of 0.001 s (shown in Fig. 2). A triangular pulse with a maximum power deposition of 3.0E05 Watts is applied to simulate the input power in one cycle. The electron temperature dose not exhibit a similar triangular pulse because the heating rate of electrons in strong electric field is nonlinear. The electron temperature gradually increases in the plasma pulse and sharply decreases as soon as the input energy ends. For typical cases, the maximum electron temperature could reach up to 3-4 eV. This value corresponds with that in experimental and numerical studies. Due to the delay of energy transformation to the electrons, molecules, radicals and other particles, the behaviour of plasma catalysis in our modelling is complicated which will be discussed in the following sections.



Fig. 2. The plasma power deposition (a) and the electron temperature (b) for the plasma pulse (before the dashed line) and afterglow (after the dashed line).



Fig. 3. Summary of number density of reactants and main products after the plasma power pulse.

Fig. 3 summarizes the number density of reactants and main products in one plasma power pulse. Besides the unreacted CO_2 and CH_4 , the syngas (H₂ and CO) is the main gas products while C_2H_6 is observed to have the highest number density among C_2 hydrocarbons (C_2H_6 ,

 C_2H_4 and C_2H_2). Since the combination of transient structures (such as O, H, CH₃, CO, OH) derived from CO₂ and CH₄ activation, liquid oxygenated molecules are form in the plasma surroundings. Alcohols (e.g. CH₃OH, C_2H_5OH and etc.) and acids (e.g. HCOOH, CH₃COOH and etc.) are found to be the major oxygenates in our simulations.



Fig. 4. Summary of number density of key intermediates (radicals) in the plasma power pulse.

Fig. 4 presents the key radicals generated in the plasma power pulse. First, H and CH_x have the highest number density because they are dissociated direct from CH₄. It is worth to mention that the number density of O is significantly lower than H and CH_x not only attribute to the consumption rate of CO2 in the plasma but also due to further recombination with other species. The CH₃ radicals can also be further dissociated in which more H and CH₂ species are generated. This process explains why H is so abundant in the plasma surroundings from another side. Subsequently, those primary species participate in the formation of products or other intermediates. C₂H₃ and C₂H₅ are found to play a critical role in the simulations which will be discussed in detail in the following sections. Last but not least, H is able to combine with O, CO, CO₂ and etc. to form OH, COOH and etc., whose density is not as high as primary species. CH_xO (x=1, 2, 3) radicals are considered to be key transient states which provide reaction path to produce oxygenates, water and syngas.



Fig. 5. The Arrhenius plot for the plasma assisted dry reforming without catalyst.

Apparent Arrhenius activation energies without catalyst, over catalyst are shown in Fig. 4 and Fig. 5. The plasma process exhibits a typical Arrhenius behaviour and the activation energy of CO₂ and CH₄ are estimated to be 55.41 kJ mol⁻¹ and 58.65 kJ mol⁻¹. It is critical to mention that the activation energy decreases after introducing the surface reactions on the Rh sites. The activation energy of CO₂ and CH₄ decrease to 42.97 kJ mol⁻¹ and 48.65 kJ mol⁻¹ respectively due to the interactions of plasma and catalysts. Compared with plasma process, the activation energy decreases up to 22.45% and 16.90% respectively.



Fig. 6. The Arrhenius plot for the plasma assisted dry reforming over Rh-based catalyst.

4. Conclusion

This work reported a chemical kinetic simulation method for plasma-catalytic dry reforming that ignores the configuration of plasma reactor and the structure of catalysts. Rate constants, reaction rates and other kinetic data were thus obtained by applying a zero-dimension PSR model to dry reforming with Chemkin software. Under a maximum electron temperature equal to 3-4 eV, value in accordance with some published experimental studies, apparent Arrhenius activation energies with and without catalyst were successively calculated. Thus, the activation energy of CO_2 and CH_4 decreased from 55.41 kJ mol⁻¹ and 58.65 kJ mol⁻¹ to 42.97 kJ mol⁻¹ and 48.65 kJ mol⁻¹ respectively, thanks to the contribution of the solid catalyst in contact with the plasma.

5. References

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