catalysts

Editorial

Editorial Catalysts: Special Issue on Plasma Catalysis

Annemie Bogaerts

Research Group PLASMANT, Department of Chemistry, University of Antwerp, Universiteitsplein 1, BE-2610 Wilrijk-Antwerp, Belgium; annemie.bogaerts@uantwerpen.be

Received: 14 February 2019; Accepted: 20 February 2019; Published: 21 February 2019

Plasma catalysis is gaining increasing interest for various gas conversion applications, such as CO_2 conversion into value-added chemicals and fuels, N_2 fixation for the synthesis of NH_3 or NO_x, and CH_4 conversion into higher hydrocarbons or oxygenates [1,2]. In addition, it is widely used for air pollution control (e.g., volatile organic compound (VOC) remediation) and waste gas treatment [3–6]. Plasma allows thermodynamically difficult reactions to proceed at an ambient pressure and temperature because the gas molecules are activated by energetic electrons created in the plasma. Plasma is indeed very reactive, being a cocktail of many different types of reactive species (electrons, various ions, radicals, excited species, besides neutral gas molecules), but for this reason, it is not really selective. Therefore, a catalyst is needed to improve the selectivity towards the production of targeted compounds.

In spite of the growing interest in plasma catalysis, the underlying mechanisms of the (possible) synergy between plasma and catalyst are not yet fully understood [7]. Indeed, these mechanisms are quite complicated, as the plasma will affect the catalyst and vice versa [1,7,8]. Moreover, due to the reactive plasma environment, and the fact that these reactive plasma species can interact at the catalyst surface, the most suitable catalysts for plasma catalysis will probably be different from thermal catalysts. Hence, more research is needed to better understand the plasma–catalyst interactions, in order to further improve the applications.

This special issue gives an overview of the state-of-the-art of plasma catalysis research, for various applications, including VOC abatement, tar component removal, NO_x conversion, CO_2 splitting, dry reforming of CH_4 (DRM), H_2S removal, NH_3 synthesis and NH_3 decomposition into H_2. Moreover, it also contains some papers that provide more insight into the underlying mechanisms of plasma catalysis and packed bed plasma catalysis reactors, by either experiments or modeling.

We have one review paper in this special issue, by Veerapandian et al., presenting an excellent overview of plasma catalysis for VOC abatement in flue gas, applying zeolites as an adsorbent and a catalyst [9]. The authors illustrate that zeolites are ideal packing materials for VOC removal, by cyclic adsorption plasma catalysis, due to their superior surface properties and excellent catalytic activity upon metal loading. The zeolites can be regenerated by plasma, allowing to reduce the energy cost per decomposed VOC molecule.

To better understand the plasma behavior in a packed bed dielectric barrier discharge (DBD), which is the most common configuration of plasma catalysis, Gao et al. developed a two-dimensional (2D) particle-in-cell—Monte Carlo collision (PIC-MCC) model, to study the mode transition from volume to surface discharges in a packed bed DBD operating in various N_2/O_2 mixtures [10]. The calculations reveal that a higher voltage can induce this mode transition from hybrid (volume + surface) discharges to pure surface discharges. Indeed, a higher voltage yields a stronger electric field, so the charged species can escape more easily to the beads and charge them, leading to a strong electric field along the dielectric bead surface, which gives rise to surface ionization waves. The latter enhances the reactive species concentrations on the bead surface, which will be beneficial for plasma catalysis. In addition, changing the N_2/O_2 gas mixing ratio affects the propagation speed of the surface ionization waves, which become faster with increasing N_2 content. Indeed, a higher O_2 content yields more electron impact attachment, and thus loss of electrons, causing less ionization. Furthermore, different N_2 and O_2 contents result in different amounts of electrons and ions on the dielectric bead surface, which might also affect the performance of plasma catalysis.

Although DBDs are the most convenient and widely studied plasma reactors for plasma catalysis, due to their simplicity, convenient catalyst integration, and easy upscaling, they suffer from limited energy efficiency. To identify the reactions in a DBD that might be responsible for this limited energy efficiency, Navascués et al. propose a method based on isotope labeling [11]. They applied this method to study wet reforming of CH_4, using D_2O instead of H_2O, as well as for NH_3 synthesis, using a $NH_3/D_2/N_2$ mixture. By analyzing the evolution of the labelled molecules as a function of power, they could obtain useful information about exchange events (of H by D atoms and vice versa) between the plasma intermediate species. This isotope labeling technique thus appears to be very appropriate for studying plasma reaction mechanisms.

As mentioned above, the most suitable catalysts for plasma catalysis might not necessarily be the same as for thermal catalysis, due to the presence of many different reactive plasma species. Hence, more research is needed to identify the different mechanisms related to plasma chemistry and thermal effects. Giammaria et al. developed a method to distinguish between both effects and applied it to $CaCO_3$ decomposition in argon plasma [12]. They prepared $CaCO_3$ samples with different external surface area (determined by the particle size), as well as different internal surface area (determined by the pores). As the internal surface area is not exposed to plasma, it only relates to thermal effects, while both plasma and thermal effects take place at the external surface area. The authors concluded that this application is dominated by thermal decomposition, as the decomposition rates were only affected by the internal surface changes, and slow response in the CO_2 concentration (of typically 1 min) was detected upon changes in discharge power. The authors measured a temperature rise within 80 °C for plasma power up to 6 W. In addition, they also studied the mechanism of CO_2 conversion into CO and O_2, which was found to be controlled by the plasma chemistry, as indicated by the fast response (within a few seconds) of the CO concentration upon changing plasma power. Indeed, this reaction is thermodynamically impossible without plasma. This methodology is very interesting to distinguish between thermal and plasma effects, and it would be nice to apply it also to other plasma catalysis reactions, in more reactive plasmas, which the authors indeed plan for their future work.

The other papers in this special issue focus on a particular application, and illustrate the broad applicability of plasma catalysis, for pollution control, gas conversion and destruction.

Zhou et al. studied CO_2 conversion in a packed bed DBD, using a water-cooled cylindrical DBD reactor with ZrO_2 pellets or glass beads of 1–2 mm diameter, to control the temperature [13]. Especially the ZrO_2 pellets provided good results, yielding a maximum CO_2 conversion around 50% (slightly higher for the smaller beads), compared to ca. 33% for the glass beads. The CO selectivity was up to 95%, while the energy efficiency was 7% (compared to 3% without ZrO_2 packing). The authors attributed the improved performance to the stronger electric field, and thus higher electron energy, along with the lower reaction temperature.

Michielsen et al. investigated dry reforming of methane (DRM) in a packed bed DBD, as compared to pure CO_2 splitting [14]. They reported that the packing materials, even when not catalytically activated, can already significantly affect the conversion and product selectivity. This is important to realize because the effect of the packing material is often not taken into account. α-Al_2O_3 packing yielded the highest total conversion (28%), with a high product fraction towards CO and ethane, as well as a high CO/H_2 ratio around 9. γ-Al_2O_3 gave a slightly lower total conversion (22%), but a more pronounced selectivity towards certain products. On the other hand, $BaTiO_3$ resulted in a lower conversion, in contrast to its performance in pure CO_2 splitting. In general, the trends of different packing materials obtained for DRM were different from those obtained for CO_2 splitting. Thus, it is clear that the packing materials can have a vast influence of the reaction performance, and thus, they also need specific attention.

In general, plasma-catalytic DRM is still in its infancy, because up to now, mostly thermal catalysts have been applied, which do not fully exploit the potential of plasma catalysis. Hence, more research is needed to design catalysts tailored to the plasma environment, to make profit of the reactive plasma species and their interactions with the catalyst surface, and to selectively produce value-added chemicals. On the other hand, the application of air pollution control, and specifically VOC removal, by plasma catalysis is already more advanced, as indicated by the vast amount of literature (cf. also the excellent reviews mentioned above [3–6,9]).

Jia et al. investigated toluene oxidation with CeO_2 as an adsorbent and they compared in-plasma catalysis (IPC) and post-plasma catalysis (PPC) [15]. The total, reversible and irreversible adsorbed fractions were quantified. The authors investigated the effect of relative humidity on the toluene adsorption and ozone formation, as well as the effect of specific energy input (SEI) on the mineralization yield and efficiency. The best results were obtained for IPC at the lowest SEI, i.e., lean conditions of ozone. The paper stresses the key role of ozone in the mineralization of toluene and the possible detrimental effect of moisture.

Likewise, Kong et al. studied toluene, nathalene and phenanthrene destruction (as model tar compounds) in humid N_2, in a rotating gliding arc reactor with fan-shaped swirling generator [16]. Tar destruction is one of the greatest technical challenges in commercial gasification technology. The authors studied the effect of tar, CO_2 and moisture concentrations, discharge current, and Ni/γ-Al_2O_3 catalyst on the destruction efficiency. The latter reached 95%, 89% and 84%, for toluene, nathalene and phenanthrene, respectively, at a tar content of 12 g/Nm^3, 15% CO_2, 12% moisture and 6 NL/min flow rate, yielding an energy efficiency of 9.3 g/kWh. The presence of the Ni/γ-Al_2O_3 catalyst significantly improved the destruction efficiency. The major liquid by-products were also identified.

Plasma-catalytic air pollution control also involves NO_x destruction, which was reported by Gao et al. [17]. The authors inserted Mn-based bimetallic nanocatalysts, i.e., Mn-Fe/TiO_2, Mn-Co/TiO_2, and Mn-Ce/TiO_2, in a DBD and demonstrated a clear improvement in the plasma-catalytic conversion compared to plasma alone and nanocatalyst alone. The Mn-Ce/TiO_2 catalyst was found to give the highest catalytic activity and superior selectivity, yielding a maximum NO_x conversion of about 99.5%. The authors applied various surface characterization methods, which revealed that the plasma-catalytic performance was greatly dependent on the phase compositions, explaining the superior performance of the Mn-Ce/TiO_2 catalyst.

H_2S removal is another application of plasma catalysis, which was studied by Xuan et al., for non-stoichiometric La_xMnO_3 perovskite catalysts (x = 0.9, 0.95, 1, 1.05 and 1.1) in a packed bed DBD reactor [18]. The plasma-catalytic performance was found to be much better than the results when only using plasma, reaching a maximum H_2S removal of 96%, producing mainly SO_2 and SO_3, for the $La_{0.9}MnO_3$ catalyst. The sulfur balance was 91%, with the remaining fraction probably deposited sulfur on the catalyst surface. The authors reported that the non-stoichiometric La_xMnO_3 catalyst had a larger specific surface area and smaller crystallite size than the $LaMnO_3$ catalyst and that the non-stoichiometric effect changes the redox properties of the catalyst. Indeed, a lower La/Mn ratio favored the transformation of Mn^{3+} to Mn^{4+}, generating oxygen vacancies on the catalyst surface, yielding a higher concentration of surface-adsorbed oxygen, and a lower reduction temperature.

An emerging application, gaining increasing interest in recent years, is NH_3 synthesis by plasma catalysis. This is attributed to the growing worldwide population and the associated demand for fertilizer production, in combination with the need to find alternatives for the energy-intensive Haber-Bosch process for NH_3 synthesis, which can comply with renewable energy sources. Although plasma catalysis might never become competitive with the current (large-scale) Haber-Bosch process, which has been optimized in industry for so many years, plasma-catalytic NH_3 synthesis might find some niche applications, for the decentralized fertilizer production based on renewable energy, due to the easy on-off switching of plasma, and thus its high potential as turnkey process. While most papers in literature apply DBD reactors for NH_3 synthesis, Shah et al. explored the possibility of an inductively coupled radiofrequency plasma, using Ga, In and their alloys as catalysts [19]. Ga-In alloys with 6:4 or 2:8 ratio at 50 W yielded the highest energy yield (0.31 g-NH_3/kWh) and lowest energy cost (196 MJ/mol). The authors tried to explain the results by means of optical emission spectroscopy of the plasma and scanning electron microscopy of the catalyst surface. They reported granular nodes on the catalyst surface, indicating the formation of intermediate GaN.

Finally, Wang et al. studied the opposite process, i.e., NH_3 decomposition for H_2 production [20]. The authors showed that vacuum-freeze drying and plasma calcination can improve the conventional preparation methods of the catalysts, and thus the performance of plasma-catalytic NH_3 decomposition. They reported an enhanced NH_3 conversion by 47%, and a rise in energy efficiency from 2.3 to 5.7 mol/kWh, compared to conventional catalyst preparation methods. At optimal conditions, they obtained 98% NH_3 conversion with 1.9 mol/kWh energy efficiency. The authors attributed this significant improvement to the creation of more active sites because the Co species can be highly dispersed on the fumed SiO_2 support, as well as to the stronger interaction of Co with fumed SiO_2 and the stronger acidity of the catalyst, as revealed by their experiments. This improved catalyst preparation method thus seems very promising and might also give inspiration for other plasma catalysis application.

It is obvious that excellent research is being performed worldwide on plasma catalysis for various types of reactions, including VOC decomposition, tar component removal, NO_x conversion, CO_2 splitting, DRM, H_2S removal, NH_3 synthesis, as well as NH_3 decomposition into H_2. We particularly note numerous activities by various Chinese groups, but also by groups in the US, UK, France, Spain, the Netherlands and Belgium. We can conclude that plasma catalysis is a very active field of research, with promising results for various applications. On the other hand, further research is highly needed, especially to obtain better insight in the underlying plasma-catalyst interactions, in order to develop catalysts that are tailored to the reactive plasma conditions, and to fully exploit the promising plasma catalysis synergy.

Finally, we sincerely thank all authors for their valuable contributions, as well as the editorial team of Catalysts for their kind support and fast responses. Without them, this special issue would not have been possible.

Conflicts of Interest: The author declares no conflicts of interest.

References

1. Neyts, E.C.; Ostrikov, K.; Sunkara, M.K.; Bogaerts, A. Plasma catalysis: Synergistic effects at the nanoscale. *Chem. Rev.* **2015**, *115*, 13408–13446. [CrossRef] [PubMed]
2. Chen, H.L.; Lee, H.M.; Chen, S.H.; Chao, Y.; Chang, M.B. Review of plasma catalysis on hydrocarbon reforming for hydrogen production - Interaction, integration, and prospects. *Appl. Catal. B Environ.* **2008**, *85*, 1–9. [CrossRef]
3. Kim, H.H. Nonthermal plasma processing for air-pollution control: A historical review, current issues, and future prospects. *Plasma Process. Polym.* **2004**, *1*, 91–110. [CrossRef]
4. Chen, H.L.; Lee, H.M.; Chen, S.H.; Chang, M.B.; Yu, S.J.; Li, S.N. Removal of volatile organic compounds by single-stage and two-stage plasma catalysis systems: A review of the performance enhancement mechanisms, current status, and suitable applications. *Env. Sci. Technol.* **2009**, *43*, 2216–2227. [CrossRef]
5. Vandenbroucke, A.M.; Morent, R.; De Geyter, N.; Leys, C. Non-thermal plasmas for non-catalytic and catalytic VOC abatement. *J. Hazardous Mater.* **2011**, *195*, 30–54. [CrossRef] [PubMed]
6. van Durme, J.; Dewulf, J.; Leys, C.; Van Langenhove, H. Combining non-thermal plasma with heterogeneous catalysis in waste gas treatment: A review. *Appl. Catal. B Environ.* **2008**, *78*, 324–333. [CrossRef]
7. Whitehead, J.C. Plasma-catalysis: the known knowns, the known unknowns and the unknown unknowns. *J. Phys. D Appl. Phys.* **2016**, *49*, 243001. [CrossRef]
8. Neyts, E.C.; Bogaerts, A. Understanding plasma catalysis through modeling and simulation—A review. *J. Phys. D Appl. Phys.* **2014**, *47*, 224010. [CrossRef]

9. Veerapandian, S.K.P.; De Geyter, N.; Giraudon, J.-M.; Lamonier, J.-F.; Morent, R. The use of zeolites for VOCs abatement by combining non-thermal plasma, adsorption and/or catalysis. *Catalysts* **2019**, *9*, 98. [CrossRef]
10. Gao, M.; Zhang, Y.; Wang, H.; Guo, B.; Zhang, Q.Z.; Bogaerts, A. Mode transition of filaments in packed-bed dielectric barrier discharges. *Catalysts* **2018**, *8*, 248. [CrossRef]
11. Navascués, P.; Obrero-Pérez, M.; Cotrino, J.; González-Elipe, A.R.; Gómez-Ramírez, A. Isotope labelling for reaction mechanism analysis in DBD plasma processes. *Catalysts* **2019**, *9*, 45. [CrossRef]
12. Giammaria, G.; van Rooij, G.; Lefferts, L. Plasma Catalysis: Distinguishing between Thermal and Chemical Effects. *Catalysts* **2019**, *9*, 185. [CrossRef]
13. Zhou, A.; Chen, D.; Ma, C.; Yu, F.; Dai, B. DBD plasma-ZrO_2 catalytic decomposition of CO_2 at low temperatures. *Catalysts* **2018**, *8*, 256. [CrossRef]
14. Michielsen, I.; Uytdenhouwen, Y.; Bogaerts, A.; Meynen, V. Altering conversion and product selectivity of dry reforming of methane in a dielectric barrier discharge by changing the dielectric packing material. *Catalysts* **2019**, *9*, 51. [CrossRef]
15. Jia, Z.; Wang, X.; Foucher, E.; Thevenet, F.; Rousseau, A. Plasma-catalytic mineralization of toluene adsorbed on CeO_2. *Catalysts* **2018**, *8*, 303. [CrossRef]
16. Kong, X.; Zhang, H.; Li, X.; Xu, R.; Mubeen, I.; Li, L.; Yan, J. Destruction of toluene, napthalene and phenanthrene as model tar compounds in a modified rotating gliding arc discharge reactor. *Catalysts* **2019**, *9*, 19. [CrossRef]
17. Gao, Y.; Jiang, W.; Luan, T.; Li, H.; Zhang, W.; Feng, W.; Jiang, H. High-efficiency catalytic conversion of NO_x by the synergy of nanocatalyst and plasma: Effect of Mn-based bimetallic active species. *Catalysts* **2019**, *9*, 103. [CrossRef]
18. Xuan, K.; Zhu, X.; Cai, Y.; Tu, X. Plasma oxidation of H_2S over non-stoichiometric La_xMnO_3 perovskite catalysts in a dielectric barrier discharge reactor. *Catalysts* **2018**, *8*, 317. [CrossRef]
19. Shah, J.R.; Harrison, J.M.; Carreon, M.L. Ammonia plasma-catalytic synthesis using low melting point alloys. *Catalysts* **2018**, *8*, 437. [CrossRef]
20. Wang, L.; Yi, Y.H.; Guo, H.C.; Du, X.M.; Zhu, B.; Zhu, Y.M. Highly dispersed Co nanoparticles prepared by an improved method for plasma-driven NH_3 decomposition to produce H_2. *Catalysts* **2019**, *9*, 107. [CrossRef]