

## A reflection on rational design of catalysts for non-thermal plasma (NTP) catalysis

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The hybrid NTP-catalytic systems are very promising for promoting various challenging catalytic chemistries. The unique activation in gas discharge via electron impact dissociation and energisation can be efficient to promote the activation of many stable and/or inert molecules such as CO<sub>2</sub> and N<sub>2</sub>, being able to drive the desired transformation of these molecules in energy efficient manners. Importantly, being different from the conventional thermocatalysis, induction time of NTP-catalysis is significantly shorter, making the hybrid NTP-catalytic system be switched on and off readily. Hence, NTP-catalysis is compatible with the intermittent renewable energy sources such as wind and solar power, being a promising tool to enable the distributed chemical storage of non-dispatchable renewable energy. However, to date catalyst design with carefully consideration of the features of NTP activation was less achieved. In this presentation, we revisited our previous research critically to comment on the rational and irrational aspects of these studies regarding catalyst design for selected NTP-catalytic systems, that is, CO<sub>2</sub> methanation, dry reforming of methane with CO<sub>2</sub>, and NH<sub>3</sub> synthesis.

Based on the reflection,<sup>[1]</sup> the following thoughts were extracted which can be beneficial to colleagues in relevant fields to finally achieve the rational design of bespoke catalysts for improving NTP-catalysis.

- NTP activation is different from conventional thermocatalysis, especially gas phase conversions. In NTP catalysis, presumably reactant molecules are activated in gas discharge, and the resulting reactive species can be short-lived. Hence, diffusion of such short-lived reactive species needs to be minimised to allow their interaction with a catalyst surface. Note that this aspect can be very important in NTP-catalysis since in such a system the catalyst surface is relatively cold (in comparison with a thermocatalytic system), which is unlikely to facilitate the dissociation of reactant molecules. Hence, the accessibility of catalytically active sites to plasma-induced reactive species should be one of the priority considerations in the catalysts design for NTP-catalysis.
- Regarding catalysis, it means surface reactions regardless in thermal or NTP systems, and thus catalyst design for NTP catalysis should be based on the relevant thermocatalytic counterparts (e.g., Ru catalyst for NH<sub>3</sub> synthesis and Ni catalyst for reforming reactions).

However, under NTP conditions the temperature of the catalyst surface can be significantly lower than that in a thermocatalytic counterpart, hence, catalyst design to ensure the activity and selectivity of a 'cold catalyst surface' may be beneficial to relevant NTP-catalytic systems.

- A good understanding of the reaction mechanisms and their changes in relation to the variation of process conditions are important aspects as well for guiding the catalyst design. Therefore, relevant mechanistic and kinetic studies correlating with the catalysts design are needed to progress our understanding.
- Catalyst design for NTP-catalysis cannot accept the existing experience in thermocatalysis without reservation. Common catalyst deactivation mechanisms such as coke formation and deposition, metal sintering, leaching and fouling, and poisoning of the catalyst surface might be avoided to some extents under NTP conditions. Therefore, relevant design strategies to address these issues might not be appropriate to be adopted by NTP catalysis. This aspect deserves special attention to avoid relevant 'pitfalls' in future research, i.e., do not propose the solutions to address the problems do not exist in NTP-catalysis.
- Considering the aspects above, both the catalyst architecture and active catalytic sites need to be engineered carefully for designing bespoke catalysts for NTP-catalysis. For example, highly dispersed metallic sites within a porous support may not be preferred by a NTP-catalytic system since (i) plasma discharge cannot be generated within the micro-/meso-porous catalyst and (ii) plasma-induced energetic species can be quenched during diffusion. Therefore, the metallic sites within cannot be fully utilised.
- Plasma discharge can activate reactant molecules to enable the desired conversions, yet it can be a double-edged sword to decompose the target products as well. Hence, if possible, regarding to the chemistry with this nature catalyst design also needs to consider this aspect to avoid the product decomposition and improve the process efficiency.

### References

- [1] X. FAN\* *et. al*, Catal. Today **419**, 114144 (2023)