

Editorial

Non-Thermal Plasma-Assisted Catalytic Reactions for Environmental Protection

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“Non-thermal plasma technology” (NTP) has notably increased. NTP is a gas ionized by an externally applied electric field. In these conditions, the electrons, due to their small mass, are usually at temperatures of the order of 105 K, whereas background gas molecules are close to room temperature. NTP can be generated in atmospheric pressure discharges—pulsed corona, pulsed glow discharge, micro-hollow cathode discharge, dielectric barrier discharge, radiofrequency (RF) discharge, and microwave discharge and generally contains ions, electrons, radicals or molecules with very high reactivity. NTP exhibit higher selectivity compared to thermal plasma-based systems and are a very active research area devoted to the intensification of chemical processes, as well as to environmental depollution. This special issue is focused on “Non-thermal Plasma Assisted Catalytic Reactions for environmental protection”, featuring the state-of-the-art in this field. For example, an interesting approach in catalyst-assisted non-thermal plasma reactions involves the selective catalytic reduction (SCR) of nitric oxide (NO) using a combination of NTP and an Mn-Cu/ZSM5 catalyst with ammonia (NH₃) as a reductant [1]. In this case the experimental results illustrate that the plasma-assisted SCR process enhances the low-temperature catalytic performance of the Mn-Cu/ZSM5 catalyst significantly, and it exhibits an obvious improvement in the NO removal efficiency. In particular, the reaction temperature is maintained at 200 °C in order to simulate the exhaust temperature of a diesel engine, and the 10% Mn-8% Cu/ZSM5 catalyst shows the highest NO removal performance with about 93.89% at an energy density of 500 J L⁻¹ and the selectivity to N₂ is almost 99%. Another important aspect that emerged from the studies reported in this special issue is the possibility of carrying out reactions of ammonia synthesis through plasma assisted by catalysis, paying particular attention to an aspect that is sometimes overlooked, namely the technical and economic feasibility of the plasma-catalytic synthesis of ammonia [2]. In this study the feasibility of plasma-catalytic ammonia is assessed for small-scale ammonia synthesis. From a comparison with the conventional Haber–Bosch process, it follows that the synthesis of plasma catalytic ammonia cannot compete with the conventional process even in the best scenario. Plasma catalysis potentially has a fast response to intermittent renewable electricity, although low pressure absorbent-enhanced Haber–Bosch processes are also expected to have fast responses to load variations. Low-temperature thermochemical ammonia synthesis is expected to be a more feasible alternative to intermittent decentralized ammonia synthesis than plasma-catalytic ammonia synthesis due to its superior energy efficiency. Again with reference to the synthesis of ammonia, in this special issue a novel ammonia synthesis process, based on the catalytic non-thermal plasma from N₂ and H₂ using Ni/γ-Al₂O₃ over Fe/γ-Al₂O₃ and Ru/γ-Al₂O₃ as catalysts, has been proposed [3]. The activity sequence was Ni/Al₂O₃ > Al₂O₃ > Fe/Al₂O₃ > no additive > Ru/Al₂O₃, surprisingly indicating that the loading of Fe and Ru decreased the activity of Al₂O₃. The catalytic activity of Ni/Al₂O₃ was dependent on the amount of loaded Ni, the calcination temperature, and the reaction time. In particular, it was observed that the NiO species was readily reduced to Ni metal in the plasma reaction, whereas the NiAl₂O₄ species was difficult to reduce. The



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P_{N_2}/P_{H_2} ratio dependence and rate constants of formation and decomposition of ammonia were finally determined for 5.0 wt% Ni/ Al_2O_3 calcined at 773 K. The ammonia yield was 6.3% at an applied voltage of 6.0 kV. Non-thermal plasma combined with wood fiber has been investigated for the diesel exhaust purification [4]. The combination of dielectric barrier discharge (DBD) and wood fiber (WF) enhanced the removal efficiency of nitrogen oxide (NO_x) owing to the positive activity of oxygen-containing functional groups (such as O–H groups or C–O groups) on the wood surface, which promoted the removal of NO_x by 10–13%. In particular, it was observed that, when carbon black was loaded on the wood fiber, there was simultaneous removal of carbon soot and NOX. Furthermore, plasma is highly effective at maintaining high catalyst activity which increases with the promotion of terrace sites at the expense of step sites [5]. It has been suggested that the concentration of such sites can be increased by high-voltage pulsed discharges as well as by microwave or gliding arc discharges. Starting from these considerations, a study of novel silica supported catalysts, which generate plasma under microwave irradiation resulting in nitric oxide and nitrogen dioxide (NO_x) production from air has been proposed in this special issue. These catalysts have either spinel- or perovskite-structures. In this process, spinel- or perovskite-type catalysts are reduced by nitrogen (even in the presence of oxygen when air is used) through lattice oxygen abstraction and NO_x generation. This reduction process takes place simultaneously with plasma generation when the catalyst is subjected to microwave radiation. In this process, reactive separation of air occurs in which N_2 can then be used in ammonia (NH_3) synthesis. In the next stage, spinel- or perovskite-catalysts are re-oxidized (catalyst regeneration) with water as oxidant to produce H_2 for use in ammonia production. Therefore, through a chemical looping process, it is possible to obtain both nitric acid (HNO_3) and NH_3 as well as NH_4NO_3 fertilizers from air and water using electricity as a processing energy. The performance of cold plasma reactor could be optimized through the use of a structured catalyst. One of the papers presented in this special issue proposed the use of Fe_2O_3 catalyst, immobilized on glass spheres, in a DBD reactor for the optimization of the performance of the cold plasma technology in the discoloration and mineralization of “acid orange 7” (AO7) azo dye in aqueous solution [6]. Thanks to the presence of the catalytic packed material, the complete discoloration and mineralization of the dye was achieved with voltage equal to 12 kV, lower than those generally used with this technology (approximately 20–40 kV). Moreover, the presence of catalyst avoids by-products formation. The immobilization of Fe_2O_3 on glass spheres allows the reuse of the structured catalyst for different cycles. Another interesting solution to increase the removal of pollutants was provided by the reverse-flow non-thermal plasma reactor coupled with catalyst and used for the abatement of toluene [7]. In this study, the toluene degradation performance of different reactors was compared under the same conditions. The mechanism of toluene abatement by non-thermal plasma coupled with catalyst was explored, combined with the generation of ozone (O_3), NO_2 , and organic by-products during the reaction process. It was found that a long reverse cycle time of the reactor and a short residence time of toluene decreased the internal reactor temperature, which was not beneficial for the degradation of toluene. A pin-type corona discharge-coupled Pd/ZSM-5 catalyst was proposed for the adsorption and plasma-catalytic oxidation of dilute ethylene [8]. The removal of ethylene in the plasma catalyst was carried out by cyclic operation consisting of repetitive steps: (1) adsorption (60 min) followed by (2) plasma-catalytic oxidation (30 min). The ethylene adsorption performance of the catalyst was improved by the cyclic plasma-catalytic oxidation. There was a slight decrease in catalyst adsorption capability with an increased number of adsorption cycles due to the incomplete release of CO_2 during the plasma-catalytic oxidation step. In particular, with cyclic plasma treatment the input energy requirement was 225 J/L, which is half that of the continuous plasma-catalytic oxidation. An important aspect that emerged from the studies reported in this special issue also concerns the distribution of the surface electrical discharge and consequently the effect of the streamer propagation direction in the catalytic pores during the catalytic plasma degradation of pollutants [9]. To predict the results, it is possible to

use a Monte Carlo collisions model to explore the effect of lateral voltage on streamer enhancement and streamer propagation control for different driving voltages in pores of various shapes, sizes, and numbers. The results demonstrate that the surface and volume discharge enhancement phenomena become more significant and streamer propagation is more restricted within a narrow channel as the lateral voltage (with the same values on the left and right sides) increases from -5 kV to -30 kV for a fixed driving voltage of -20 kV. Moreover, it was observed that the increase of the number or size of the pores enhances both the volume and surface discharges. The addition of a heterogeneous TiO_2 -based catalyst can be efficient in the degradation of pharmaceutical compounds present in aqueous solution such as acetylsalicylic acid [10]. Furthermore, the addition of hydrogen peroxide increased the rate of acetylsalicylic acid degradation, but injecting an excess decreased the degradation rate due to a scavenger effect. Although there was an initial increase in the decomposition efficiency by the addition of TiO_2 powder, the addition of an excessive amount inhibited the generation of plasma and decreased the degradation rate. The simultaneous addition of H_2O_2 and TiO_2 powder resulted in the highest degradation efficiency. Finally, an interesting review about the catalytic formulations coupled with non-thermal plasma technology used for water pollutants removal is reported in this special issue [11]. From this review, several important aspects related to the use of catalysts coupled to the non-thermal plasma process such as the type of catalyst, the optimal reactor configuration, and also economic aspects, have emerged. In particular, it was noted that the combination of NTP with heterogeneous catalysts allows better performance. With regards to the reactor configuration, the DBD type seems to be the most used when the catalyst is coupled to the NTP process because the DBD configuration allows suitable positioning of the catalyst, very close to the discharge zone. Moreover, in order to use this kind of reactor configuration the catalyst configuration is also important. In fact, it was observed that in the case of DBD reactor, the ideal solution could be the use of a structured catalyst. This is an advantageous choice for two reasons: the first, that of guaranteeing the optimal arrangement of the catalyst, which would be “blocked” in the discharge zone; the second relates to the possibility of easily separating the catalyst at the end of the treatment and being able to reuse it for different process cycles. Some important considerations have also been made regarding the energy yield of this system, evidencing that by increasing the input voltage, improvements in terms of degradation efficiency are not always observed. This result indicated that a “waste” of energy can be observed which makes the process, as a whole, not economically convenient. Moreover, comparing the energy efficiency between NTP and NTP coupled with a catalyst, it can be stated that adding a catalyst in the DBD reactor could help make the process economically sustainable. It is interesting to note that the non-thermal plasma is able to regenerate the catalyst inserted in the reactor and it is worthwhile to note that compared with other advanced oxidation processes (AOPs), NTP combined with catalysts needed to shorter reaction time, resulting in a higher reactive species production. Thus, it is possible to confirm that the presence of a catalyst allows some limitations in industrial applications to be overcome since it is able to regulate selectivity towards the desired products. The contribution given by the authors of these papers to the special issue was, therefore, essential to understand several important aspects related to the use of catalysts in the non-thermal plasma process. For this reason, we want to express our sincere thanks to all the authors for their valuable contribution and also to the Catalyst editorial team for their constant and kind support. Without them, the realization of this special issue would not have been possible.

References

1. Zhu, T.; Zhang, X.; Niu, W.; Liu, Y.; Yuan, B.; Li, Z.; Liu, H. Selective Catalytic Reduction of NO by NH_3 Using a Combination of Non-Thermal Plasma and Mn-Cu/ZSM5 Catalyst. *Catalysts* **2020**, *10*, 1044. [[CrossRef](#)]
2. Rouwenhorst, K.H.; Lefferts, L. Feasibility study of plasma-catalytic ammonia synthesis for energy storage applications. *Catalysts* **2020**, *10*, 999. [[CrossRef](#)]

3. Iwamoto, M.; Horikoshi, M.; Hashimoto, R.; Shimano, K.; Sawaguchi, T.; Teduka, H.; Matsukata, M. Higher Activity of Ni/ γ -Al₂O₃ over Fe/ γ -Al₂O₃ and Ru/ γ -Al₂O₃ for Catalytic Ammonia Synthesis in Nonthermal Atmospheric-Pressure Plasma of N₂ and H₂. *Catalysts* (2073–4344) **2020**, *10*.
4. Guo, X.; Ha, K.H.; Du, D. New Experiment of Diesel Exhaust Treatment by Atmospheric Pressure Plasma–Wood Fiber Combination. *Catalysts* **2020**, *10*, 577. [[CrossRef](#)]
5. Akay, G. Plasma Generating—Chemical Looping Catalyst Synthesis by Microwave Plasma Shock for Nitrogen Fixation from Air and Hydrogen Production from Water for Agriculture and Energy Technologies in Global Warming Prevention. *Catalysts* **2020**, *10*, 152. [[CrossRef](#)]
6. Iervolino, G.; Vaiano, V.; Pepe, G.; Campiglia, P.; Palma, V. Degradation of Acid Orange 7 Azo Dye in Aqueous Solution by a Catalytic-Assisted, Non-Thermal Plasma Process. *Catalysts* **2020**, *10*, 888. [[CrossRef](#)]
7. Liang, W.; Sun, H.; Shi, X.; Zhu, Y. Abatement of Toluene by Reverse-Flow Nonthermal Plasma Reactor Coupled with Catalyst. *Catalysts* **2020**, *10*, 511. [[CrossRef](#)]
8. Saud, S.; Nguyen, D.B.; Kim, S.-G.; Lee, H.W.; Kim, S.B.; Mok, Y.S. Improvement of Ethylene Removal Performance by Adsorption/Oxidation in a Pin-Type Corona Discharge Coupled with Pd/ZSM-5 Catalyst. *Catalysts* **2020**, *10*, 133. [[CrossRef](#)]
9. Gu, J.-G.; Zhao, P.; Zhang, Y.; Wang, H.-Y.; Jiang, W. Discharge Enhancement Phenomenon and Streamer Control in Dielectric Barrier Discharge with Many Pores. *Catalysts* **2020**, *10*, 68. [[CrossRef](#)]
10. Bang, H.-J.; Lee, H.; Park, Y.-K.; Ha, H.-H.; Yu, Y.H.; Kim, B.-J.; Jung, S.-C. Assessment of Degradation Behavior for Acetylsalicylic Acid Using a Plasma in Liquid Process. *Catalysts* **2019**, *9*, 965. [[CrossRef](#)]
11. Russo, M.; Iervolino, G.; Vaiano, V.; Palma, V. Non-Thermal Plasma Coupled with Catalyst for the Degradation of Water Pollutants: A Review. *Catalysts* **2020**, *10*, 1438. [[CrossRef](#)]