Review and Discussion on the Use of Plasma for Catalyst Regeneration

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Abstract: Most of researches reported in the field of plasma catalysis focused on the reaction characteristics such as enhanced reactivity and possible control of product selectivity. Because of that, regeneration of catalyst by plasma has not drawn much attention so far. However, regeneration of catalyst does not require tight condition for process cost that is severe issue in reaction control by plasma catalysis, and have more room for possible synergistic effect by applying plasma. Plasma can provide low temperature activation for regeneration reactions and provide effective tool for a heating. In this presentation, cases of catalyst regeneration by plasma in diverse aspects of catalyst deactivation are introduced with regeneration mechanism and perspective of the technology.

Keywords: Regeneration, Catalyst, Plasma

1. Introduction

Application of plasma has been studied for the possible synergistic effect. Expected synergistic effect includes enhanced conversion, increased selectivity of products, brand new reaction paths that is not achievable by existing catalytic reaction. However, application of plasma for the catalytic reaction always confronts issues of cost effectiveness and existence of synergistic effect itself. Actually, application of plasma for the catalytic process should be considered in overall stages of catalyst utilization or from the stage of catalyst preparation, reaction and finally, regeneration of catalyst itself. Different with “reaction” stage, preparation and regeneration of catalyst does not invoke severe issue of cost effectiveness but has more room for synergistic effect. In this presentation, selected cases of catalyst regeneration by plasma is introduced with proposed mechanism of regeneration. Also, a prospect of plasma application for the regeneration of catalyst is provided.

2. Deactivation of catalyst

Aspects of deactivation of catalyst can be sorted by deactivation mechanism or one by physical, chemical, thermal. Among these, physical deactivation cannot be regenerated except fouling and has nothing to do with plasma. So, selected types of deactivation except crushing and physical fragmentation are listed below.[1]

- Carbon deposition: carbon deposition results in physical deposition of catalytic site or micro-pores and are mostly observed in the conversion of hydrocarbon species such as hydrogenolysis, cracking, reforming F.-T. process
- Oxidation : oxidation of metallic catalyst results in removal of catalytic site and observed in the reaction accompanying oxidative function
- Poisoning : poisoning occurs mostly by unexpected impurities such as sulphur, sodium, phosphate and so on. These impurity occupies active site reduces reactivity.
- Sintering : when catalyst is exposed high temperature condition, small cluster of catalyst agglomerates resulting in reduction of active sites
- Fouling by solid: side reaction often produces by product in solid phase. Mostly are in salt that physically covers catalytic surface.

3. Cases of catalyst regeneration by plasma

3.1 Reduction of oxidized catalyst

Figure 1 shows comparison of TPR (temperature programmed reduction) pattern in CuO reduction to Cu by thermal and plasma method.[2] Clearly, use of plasma lowers the temperature of reduction and accelerates the time of full reduction of the oxidized catalyst.

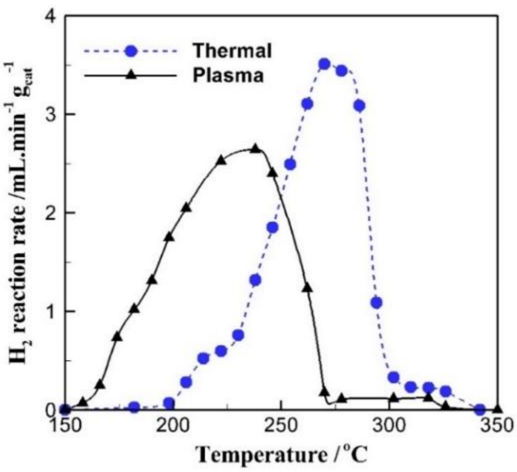

Figure 1. Comparison of H2 TPR pattern in thermal and plasma reduction [34]

3.2 Regeneration from poisoning by HC species

In low temperature oxidation process such as CO oxidation in low temperature condition, HC species in the stream possibly cannot oxidized and can be deposited on the catalyst surface. In plasma-catalytic reactor, plasma generated ozone and reactive species can remove the poisoning species. Application of plasma in the catalytic site can induce different result with simple ozone injection as shown in Fig.2.[3]

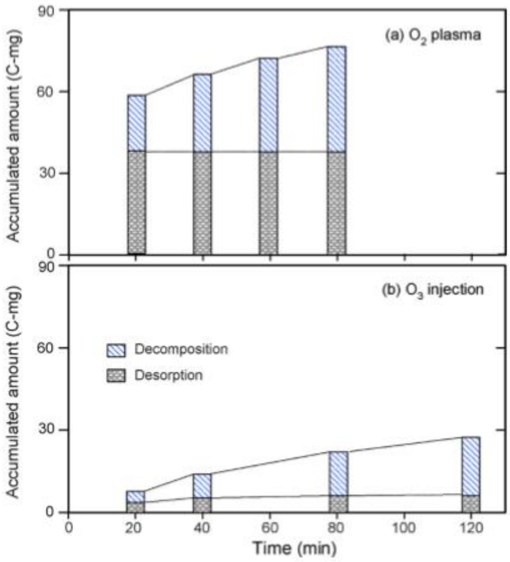

Figure 2. Accumulated carbon from decomposition and desorption during the regeneration.[3]

3.3 Regeneration from carbon deposition

Carbonaceous deposits can be formed in the course of combustion, hydrogenolysis, pyrolysis, reforming and so on. [1] Carbonaceous deposited should be oxidized or burned out for the removal. Regeneration of DPF (Diesel Particulate Filter) is one of a good case of that. Plasma can be used as a burner for the elevation of the exhaust stream temperature. Figure 3 shows plasma DPF system for the field test. [4]

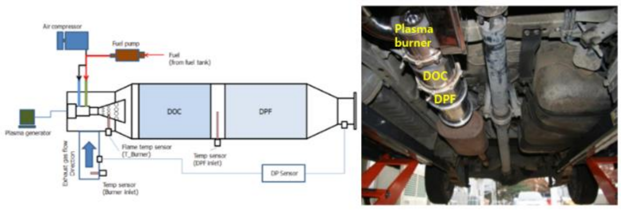

Figure 3. Schematic (left) and photograph (right) of Plasma burner for DPF regeneration. (reproduced from [4])

3.3 Removal of fouling (ABS in SCR catalyst)

ABS (Ammonium Bi-Sulfate) is produced in the SCR reaction in low temperature condition. Typical temperature condition of SCR is above 300ºC and does not confront the formation of ABS. However, in the case of low temperature environment such as low speed marine engine, ABS should be periodically removed. Reversible reaction of ABS formation can be utilized.[5] High temperature condition can decompose ABS and the SCR catalyst requires tools for the heating up the catalyst. Plasma burner can be a cost effective tools of catalyst regeneration. Figure 4 shows regeneration of SCR catalyst by plasma burner [6]

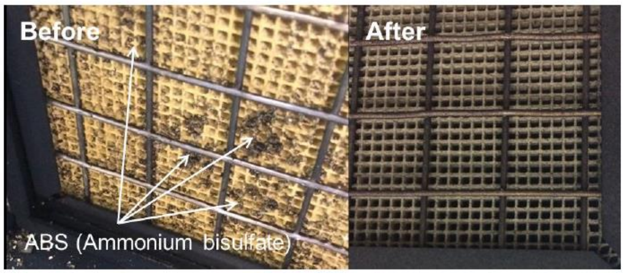

Figure 4. Before and after regeneration of ABS on SCR catalyst

3. Mechanism of plasma regeneration

4.1 Effective supply of oxidant/reductant

Oxidative function can be provide by plasma via active oxygen species such as ozone. In-plasma type and after-plasma type can provide different oxidative function because direct transfer of short-lived oxygen species can be utilized in in-plasma configuration. Most important benefits of plasma oxidation is lower temperature condition for the oxidation. High temperature condition for typical thermal oxidation (also for thermal reduction) ca induce sintering of the catalyst in the course of regeneration. But plasma can provide regeneration in a lower temperature condition.

Likewise regeneration by oxidation, effective reductant also can be provided by plasma. In the hydrogen discharge, gas phase H radical can be supplied to the catalytic surface and Eley-Rideal type reaction by gas phase H radical can accelerate the reduction process.[2]

What is remarkable here is the characteristic of low temperature oxidation. Because the oxidation is hosted in the low temperature condition, among the various deposited species, heavy molecules have possibility of incomplete oxidation resulting in secondary deactivation by deposited by-products.

4.2 Effective supply of thermal environment

Most of the regeneration of catalyst inevitably invokes thermal environment to remove deposited contaminants.

Because of that, effective way of heating is required. Plasma can be a supplier of heat. Actually plasma itself is not an effective tool for heating. Use of chemical energy by combustion is efficient way of heating. But plasma can contribute this type of regeneration. Plasma can be used as a strong mechanism for flame stability. Plasma can provide wide flammability limit. Repetitive ignition especially in AC driven plasma, reactive species and heat transfer from arc or streamer to reactant gas can provide strong means of flame stabilization. Figure 5 compares flammability in methane premixed flame with and without plasma (rotating arc) [7]

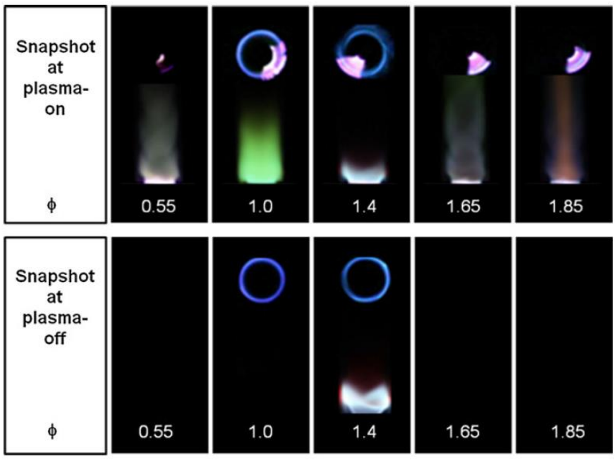

Figure 5. Comparison of flammability with/without plasma, 35W of plasma power, shutter speed of 1/4s for side view and 1/500s for top view [7]

Wide flammability can be utilized for reduced air usage on burner operation resulting in the reduction of the operation cost of the burner.

4.2 Other considerations

In plasma catalysis, there is an interaction between discharge phenomena and catalytic surface reaction. Change of catalytic surface or deactivation and regeneration process itself can possibly change the discharge environment as shown in Fig.6 or comparison of discharge in oxidized and reduced Cu catalyst. [2]

Deactivation of catalyst results in different conductivity and di-electricity and can generate different reaction path for gas phase reaction by plasma. Because of that, design of plasma application should be carefully designed both for the reaction stage and regeneration stage.

4. Summary and prospects

Several cases of plasma application are introduced with possible mechanisms under the regeneration process. Plasma catalysis is complex phenomena including surface chemistry and discharge physics. Because of that, application of plasma also should be carefully designed.

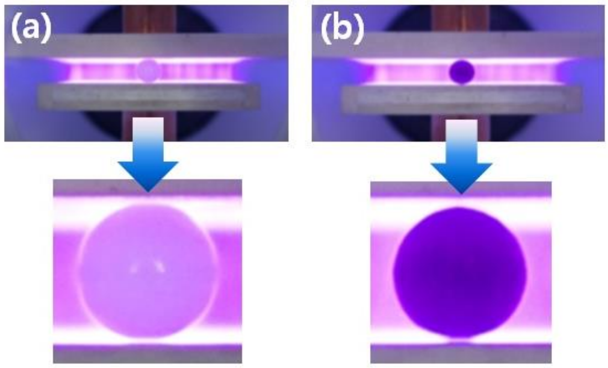

Figure 6. Comparison of single bead discharge inside DBD configuration, left for alumina bead coated with CuO, right for Cu. [2]

However, application of plasma in the regeneration step of the catalyst can give positive synergistic effect such as low temperature activation (regeneration) that can reduce possible sintering of the catalyst and cost of the reaction. Plasma burner can also be a good alternative to typical duct burner for heating up the catalyst. Plasma burner can supply high temperature with hydrogen that can be helpful for the removal of contaminants with lowered temperature of regeneration. Based on the case studies reported, more applications for the regeneration of catalyst in diverse environment can be developed.

5. References

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