

## Plasma application for more environmentally friendly catalyst preparation\*

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*Abstract:* The present status of catalyst preparation using nonthermal plasma treatment has been summarized in this paper. Improved dispersion, better low-temperature activity, enhanced stability, and better anti-carbon deposition performance can be achieved with nonthermal plasma-treated catalysts. The improvement in catalyst preparation with nonthermal plasma treatment can reduce or avoid the use of hazardous chemicals. Nonthermal plasma catalyst treatment has especially induced a new development of nonthermal plasma for catalyst reduction. The reduction using hydrogen at high temperatures or using hazardous liquid chemicals can be replaced by the developed plasma reduction process. The mechanism for nonthermal plasma treatment has been presented. An analog between the man-made gas discharge plasmas and the environment inside the zeolite pores and around catalyst surface defects is also proposed.

*Keywords:* catalysts; preparation; nonthermal plasmas; treatment; cold plasmas; plasma synthesis; gas discharge.

### INTRODUCTION

Plasma is a substance in which many of the atoms or molecules are effectively ionized. Plasma can be generated if sufficient energy is added into a gas or a gas mixture. Plasma is, thereby, known as the fourth state of matter. Some 99 % of the matter in the universe is in the plasma state. However, temperatures and pressures encountered on Earth are not favored for the formation of plasmas, except under some typical situations, such as lightning and the Northern Lights [1]. A number of methods, including combustion, flames, electrically heated furnaces, electric discharges (corona, spark, glow, arc, microwave discharge, plasma jets, and radio frequency (RF) plasma), and shocks (electrically, magnetically, and chemically driven) [2], have been applied for the generation of plasmas. For the laboratory and industrial applications, plasmas are mostly created by applying direct or alternating high voltage to a gas or a gas mixture. This is normally referred to as gas discharge plasma. Depending on the energy level, plasmas are usually classified as high- and low-temperature plasmas (including thermal and nonthermal plasmas). High-temperature plasmas are normally used for nuclear applications. Low-temperature plasmas, including thermal and nonthermal plasmas, are extremely important for the syntheses and processing of matters. Thermal plasma is plasma in which almost all its components are at thermal equi-

\*Paper presented at the 17<sup>th</sup> International Symposium on Plasma Chemistry (ISPC 17), Toronto, Ontario, Canada, 7–12 August 2005. Other presentations are published in this issue, pp. 1093–1298.

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librium. The application of thermal plasma has created a huge business of syntheses and processing of inorganic materials, including materials for catalyst application [3–11]. The nonthermal plasma has been extensively employed for processing organic materials and also been considered very promising for catalyst modification or treatment [12–15] because of its nonequilibrium properties, low power requirement, and its capacity to induce physical and chemical reactions at relatively low temperatures [3]. The electrons in nonthermal plasma can reach temperatures of 10 000–100 000 K (1–10 eV), while the gas temperature can remain as low as room temperature. It is the high electron temperature that determines the unusual chemistry of nonthermal plasmas. Nonthermal plasmas are also referred to as cold or nonequilibrium plasmas. Based upon the mechanism how plasma is generated, the pressure applied, and the electrode geometry, nonthermal plasmas can have several very different types, including glow discharge, silent discharge (or dielectric barrier discharge), and RF discharge [3]. The glow discharge is a low-pressure discharge usually operating between flat electrodes. Electrons in the glow discharge are highly energetic. The excited neutral atoms and molecules generate a typical glow, such as the one in fluorescent tubes. Recently, the atmospheric glow discharge has been developed [16]. It is expected that more applications of plasmas using glow discharge will be developed in the future. The corona discharge is an inhomogeneous discharge and can be initiated at atmospheric pressure using inhomogeneous electrode geometries, such as a pointed wire electrode with a plate one. It is the curvature of small radius point at the tip of the wire electrode that results in a high electric field needed for ionizing the neutral molecules. The silent discharge or dielectric barrier discharge combines the large excitation volume of the glow discharge with the high-pressure characteristics of the corona discharge. A dielectric layer covers at least one electrode in the silent discharge. The entire electrode area will be effective for discharge reactions. Once the silent discharge is initiated at any location within the gap between electrodes, the charge accumulates on the dielectric to form an opposite electric field and interrupts the current flow in a few nanoseconds to generate microdischarges. The duration of the current pulse is related to the pressure, properties of gases, and the dielectric material applied. The RF discharge operates at high frequencies (several megahertz) and very low pressure to achieve the nonequilibrium conditions. The RF discharge has been extensively applied in the material processing.

As mentioned above, huge businesses of inorganic material syntheses using plasma have already been successfully created. The businesses include ozone generation, syntheses of metal oxides (with specific nanostructure), nitrides, typical alloys, and many others. Recently, applications of plasmas for catalyst preparation have attracted much attention [8–15]. Catalysts have been developed for applications in chemical, energy, and environmental industries. Especially, the further development of C1 chemistry requires more effective catalysts owing to the depleting petroleum resources. Concerns about emission control also lead to a quick development of environmental catalysis. Using catalysts has become one of the worldwide-acknowledged 12 principles of green chemistry [17]. However, the present processes for preparation, regeneration, and disposal of catalysts remain as major contributors to pollution of air, water, and land. It is critical to improve the current catalyst preparation processes and to exploit novel preparation technologies simultaneously. By using plasmas, it is possible to create new catalyst materials, regenerate the used catalysts, and improve catalyst performance simultaneously. Several review articles and journal issues have presented the recent R&D status of catalyst preparation using plasmas [3,8–10]. In general, there are two ways to prepare catalysts via plasmas: one is by using thermal plasma processing or spraying; the other is by plasma treatment or modification [3]. The latter does not synthesize the catalyst directly. It just treats or modifies the catalyst or the support before, during, or after the conventional catalyst preparation steps with, mostly, nonthermal plasmas. The aim of the present work is to summarize the recent development of catalyst treatment using nonthermal plasmas according to the principles of green chemistry.

## CHARACTERISTICS OF CATALYST PREPARATION VIA NONTHERMAL PLASMA TREATMENT

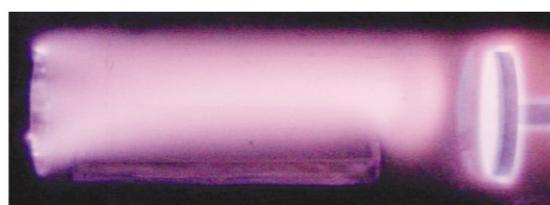
Highly energetic electrons represent the most important character of nonthermal plasmas. Although other plasma species may also present some influence during the plasma treatment, one cannot ignore the impact of electrons during nonthermal plasma treatment on the catalyst and on the precursor of the catalyst. However, the mechanism for the treatment is still far from clear. In order to determine the role of thermal effects during nonthermal plasma treatment, temperature measurements have been carefully conducted using thermal couple and infrared (IR) imaging with a portable thermal imaging camera (IRCON 100PHT). Figure 1 shows images and IR thermal image of glow discharge during the plasma treatment without and with a catalyst, respectively. As shown in Fig. 1c, the catalyst powder (40–60 mesh) is in the lowest temperature region, with a temperature of ca. 17 °C. The highest temperature of the system is just 42.4 °C, located in the region close to the cathode. The gas temperature distributions of glow discharge during the treatments of many other catalysts are similar. The results suggest that the thermal effect can be neglected during nonthermal plasma treatments. The observed improvement or enhancement in catalyst performance after plasma treatment must be due to other effects.

The challenge is: How does plasma affect the catalyst powder? Or, what exactly happened to the catalyst powder during the nonthermal plasma treatment? An electronic mechanism was proposed in our earlier study to explain the observed phenomena [18]. When immersed in the plasma zone, the particles perform as the electron sinks. Each particle can be charged up to thousands of electrons. Previous work has also shown that the presence of catalyst powders dramatically decreases the density of electrons in glow discharge due to the trapping of electrons [19]. These trapped electrons form a plasma sheath around the particle (Fig. 2a) [20]. The electron flow in the plasma exposes a strong repulsive force on the sheath. At the same time, strong Coulomb repulsions exist between the electrons trapped on the same particle (Fig. 2b) [20]. The bonds of the precursors or clusters are possibly elongated or distorted (Fig. 2c) [20] under this condition and are easily split if collided by other energetic species, resulting in a high dispersion. Further theoretical investigation is being conducted to support the proposed mechanism.

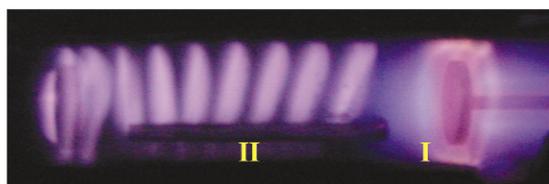
The present investigation excludes the effect of thermal chemistry during nonthermal plasma catalyst treatment. This means that we should focus on the plasma chemistry in order to understand and improve the plasma treatment process. For example, if we attempt to decide which gas should be used as a working medium for plasma catalyst treatment, we can mostly consider its discharge-related properties (e.g., dissociation energy and ionization energy) instead of the properties for thermal chemistry.

## CHARACTERIZATION OF CATALYSTS PREPARED VIA NONTHERMAL PLASMA TREATMENTS

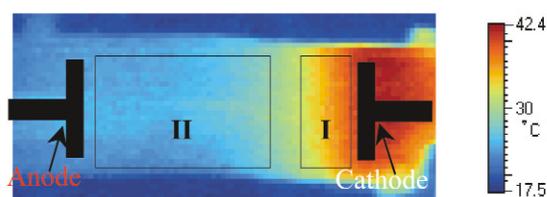
It was previously reported that the catalyst treatment using nonthermal plasmas induces increases in the catalyst acidity (both Brønsted and Lewis acidities), in the dispersion and in the low-temperature activity (which mostly benefited from the increased dispersion) [19,21–26]. For example, RF nonthermal plasma effects on the distribution of acidic sites, measured by NH<sub>3</sub>-TPD (temperature programmed deposition), are shown in Fig. 3a [26]. Both H<sub>2</sub> and O<sub>2</sub> plasmas are effective for modifying the acidic sites for NH<sub>3</sub> adsorption. But O<sub>2</sub> plasma shows a stronger effect on 1 % Pt/Al<sub>2</sub>O<sub>3</sub> and increases all sites, including weak, medium, and strong sites for NH<sub>3</sub> adsorption, while H<sub>2</sub> plasma mainly increases weak acidic sites. As an example of the plasma effect on basic sites, CO<sub>2</sub>-TPD results of calcined, H<sub>2</sub>-plasma-treated, and O<sub>2</sub>-plasma-treated 1 % Pt/Al<sub>2</sub>O<sub>3</sub> are listed in Fig. 3b. H<sub>2</sub> plasma has little effect on the population and distribution of CO<sub>2</sub> adsorption sites. On the other hand, O<sub>2</sub> plasma generates both strong and medium CO<sub>2</sub> adsorption sites on 1 % Pt/Al<sub>2</sub>O<sub>3</sub>. In addition, the combination of O<sub>2</sub> and H<sub>2</sub> plasma treatments, especially the O<sub>2</sub> plasma first followed by H<sub>2</sub> plasma, is most effective in the generation and redistribution of CO<sub>2</sub> sites. As listed in Fig. 3c, 1 h of H<sub>2</sub> plasma treatment largely reduces the strong



(a)

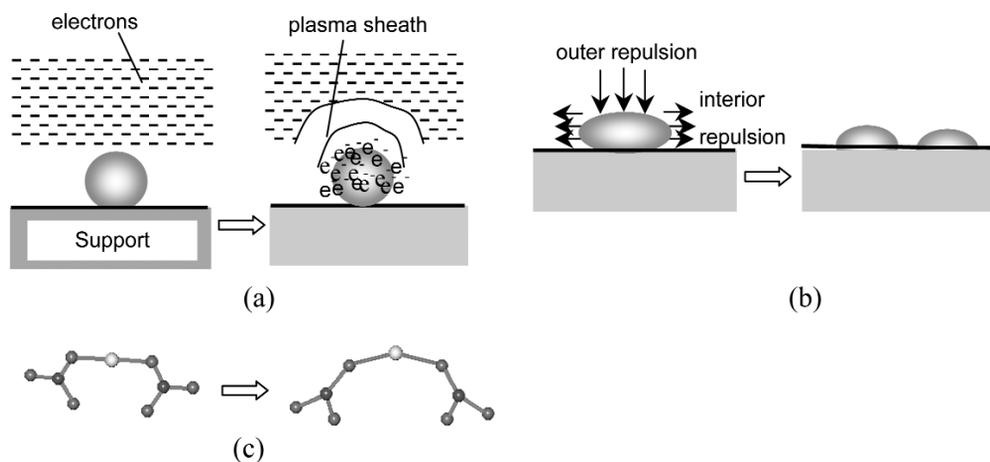


(b)

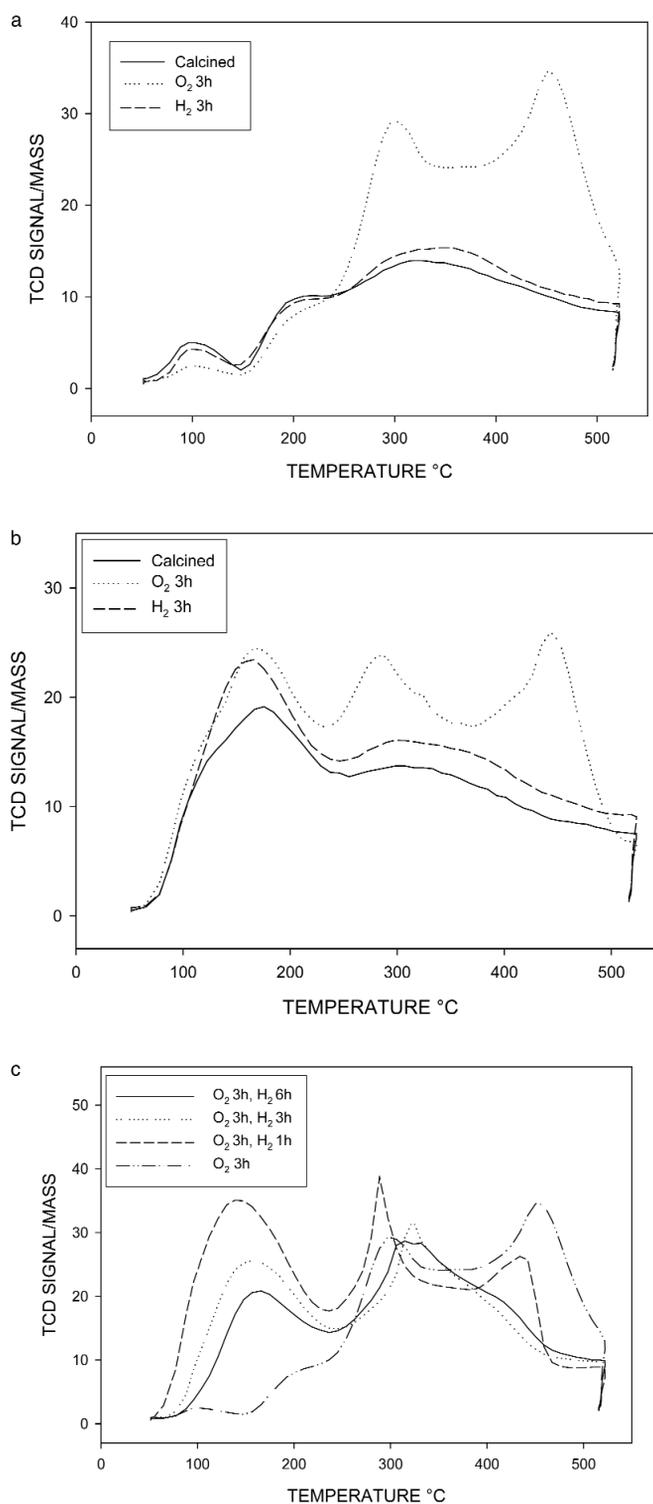


(c)

**Fig. 1** (a) Image of argon glow discharge with no catalyst powder for the comparison purpose; (b) Image of argon glow discharge during treatment of 2 % Pd/Al<sub>2</sub>O<sub>3</sub> catalyst; (c) IR thermal image of argon glow discharge during catalyst treatment. I: negative glow space; II: positive column space (catalyst powder located on the bottom). Operating parameters: plasma-reforming gas: Ar; pressure: 100 Pa; flow rate: 10 mL/min; voltage: 0.97 kV; current: 13 mA.



**Fig. 2** Mechanism for the nonthermal plasma catalyst treatment [18,20].



**Fig. 3** TPD characterization of RF plasma-treated 1 % Pt/Al<sub>2</sub>O<sub>3</sub> catalysts. (a) NH<sub>3</sub>-TPD of calcined, O<sub>2</sub>-treated and H<sub>2</sub>-plasma-treated 1 % Pt/Al<sub>2</sub>O<sub>3</sub>. (b) CO<sub>2</sub>-TPD of calcined, O<sub>2</sub>-treated and H<sub>2</sub>-plasma-treated 1%Pt/Al<sub>2</sub>O<sub>3</sub>. (c) CO<sub>2</sub>-TPD of 1 % Pt/Al<sub>2</sub>O<sub>3</sub> with combinations of O<sub>2</sub> and H<sub>2</sub> plasma treatments.

sites generated by the 3-h O<sub>2</sub> plasma treatment and simultaneously increases the sites with less strength (mainly weak sites) for CO<sub>2</sub> adsorption. As the H<sub>2</sub> plasma treatment time increases from 1 to 3 h, the strong site population further decreases and simultaneously both weak and medium sites decrease. Further increase of the H<sub>2</sub> plasma treatment time to 6 h results in a further decrease of the weak sites and with relatively no change of medium sites. The results demonstrated that plasma is powerful in generating and redistributing the acidic and basic sites that are critical to reaction activity and selectivity.

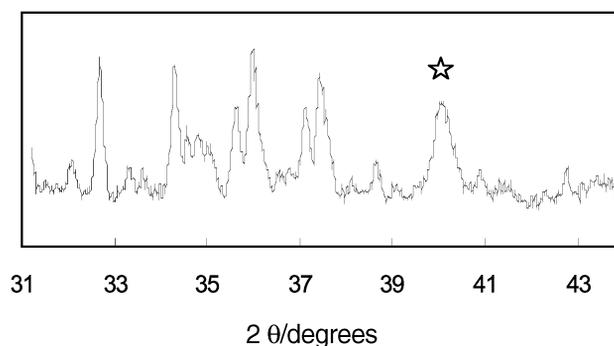
The catalyst stability can also be enhanced [22,24]. Similar results have also been obtained from the catalyst treatment using corona discharge [27], afterglow of microwave discharge [28], and RF discharge [29–31]. For example, the effect of RF plasma on the enhancement of stability of Ni catalysts for benzene hydrogenation is demonstrated in Table 1 [30]. The results in Table 1 include five different catalysts: air(A), H<sub>2</sub>(A), air(B), H<sub>2</sub>(B), and un-calcined 5 % Ni/Al<sub>2</sub>O<sub>3</sub>. The support materials with plasma treatments before impregnation are designated as (B) and the catalysts treated with plasmas are designated as (A). For example, H<sub>2</sub>(A) represents catalyst with H<sub>2</sub> plasma treatment after nickel nitrate impregnation. The activity order of five different 5 % Ni/Al<sub>2</sub>O<sub>3</sub> catalysts, reduced at 450 °C, after 8 h on stream with air(B) > H<sub>2</sub>(B), air(A) > H<sub>2</sub>(A), un-calcined, while the activity of the calcined catalyst (calcined at 500 °C) is negligible at the same condition. To determine the plasma effect on catalytic stability, an extended reduction in H<sub>2</sub> at 600 °C for 5 h was used to speed up the deactivation. The activity order of catalysts, reduced at 600 °C, after 8 h on stream is air(A), H<sub>2</sub>(A) > air(B), H<sub>2</sub>(B) > un-calcined. The relative stability of catalysts is calculated based on the percent decrease from the activity with 450 °C reduction to the activity with 600 °C reduction. As shown in Table 1, the percent decrease order for all five catalysts is H<sub>2</sub>(A) < air(A) < H<sub>2</sub>(B) < air(B), un-calcined, and the stability order is H<sub>2</sub>(A) > air(A) > H<sub>2</sub>(B) > air(B), un-calcined. The results demonstrated that both plasma treatments before and after impregnation of metal precursors are effective in improving the stability of Ni catalysts for benzene hydrogenation. However, plasma modifications after impregnation increase the stability of catalysts much more than that of catalysts with plasma modification before the impregnation.

**Table 1** Activity and stability of Ni catalysts for benzene hydrogenation at 150 °C. H<sub>2</sub>/benzene = 18/1, GHSV = 63 000 cc/g.cat/h.

Catalyst	% Benzene conversion after 8 h on stream		Percent decrease of activity
	Reduction at 450 °C	Reduction at 600 °C	
Air(B)	55.8	36.9	38.8
H <sub>2</sub> (B)	52.1	35.2	32.4
Un-calcined	46.9	29.5	37.2
Air(A)	51.2	44.2	13.6
H <sub>2</sub> (A)	46.3	43.0	7.1

From the point of view of green chemistry, the increase in the dispersion and the stability of the catalyst represents a reduction in the use of chemicals, especially the use of noble metals and precursors. The electrical energy consumption for nonthermal plasma catalyst treatments is not high. For example, in the case of glow discharge catalyst treatment [18,20–23], the energy consumption is about 1 W·h/g-catalyst and can be further reduced significantly when a large-scale treatment is established. And, the gas used for the nonthermal catalyst treatment can be argon, air, oxygen, and nitrogen, which are basically cheap and nonhazardous.

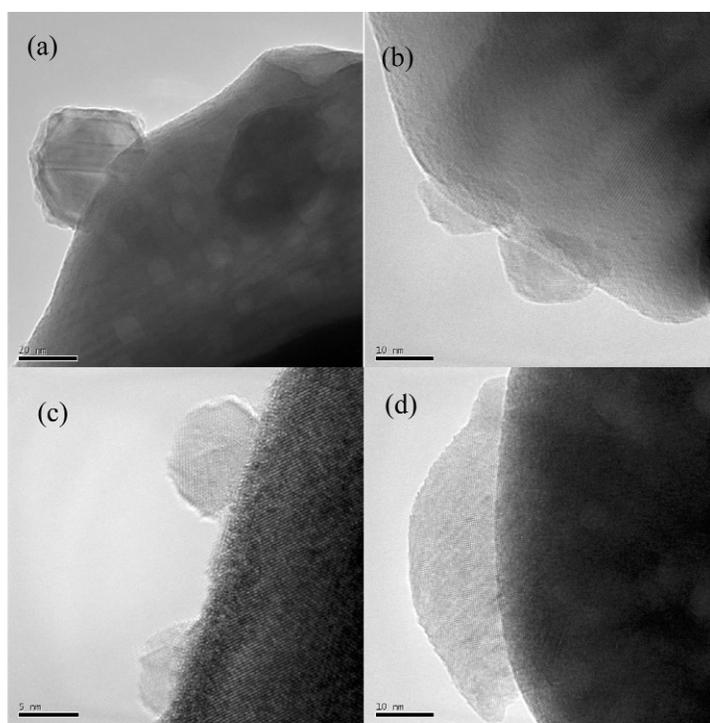
A very important potential use of plasma treatment for catalyst preparation is the reduction capability of plasma treatments. During the nonthermal plasma catalyst treatment using argon glow discharge plasma [18,21,22] and using hydrogen plasma (low-frequency ac discharge [15], RF discharge [29], and dielectric-barrier discharge [32]), the catalyst can be reduced. To further investigate the plasma reduction capability, we applied oxygen glow discharge plasmas to treat the Pd/HZSM-5 catalyst [33]. The temperature measurement, during oxygen plasma treatment, confirms the catalyst powder was at around room temperature. Figure 4 exhibits the X-ray diffraction (XRD) patterns of the oxygen plasma-treated catalyst. There is a significant peak of metallic Pd in the XRD patterns. Characterization using X-ray photoelectron spectroscopy (XPS) also confirms the existence of metallic Pd after oxygen plasma treatment, which strongly suggests that the oxygen plasma is capable of reducing catalysts at room temperature. The result is to our surprise and suggests that the plasma reduction capability is not restricted to using only reducing gases. Other gases via plasma processes are likely to have similar reducing effect, such as Ar, N<sub>2</sub>, etc., which further opens the door of “green” reduction of various industrial catalysts.



**Fig. 4** XRD patterns of oxygen glow discharge plasma treated Pd/HZSM-5 (Pd loading: 1 wt %; metallic Pd phase) [33].

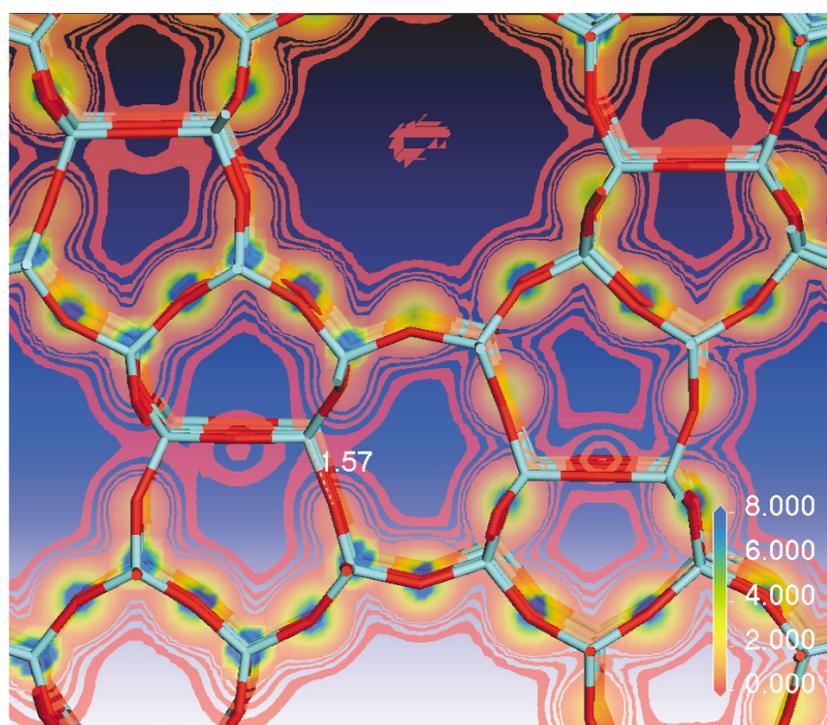
Since the plasma catalyst reduction could potentially replace the conventional catalyst reduction procedures using hydrogen or chemicals, it represents a new important R&D direction of green chemistry for alternative reagents. We have confirmed the capability of nonthermal plasmas for catalyst reduction via the plasma-reduced Pd catalyst for glucose oxidation [34]. Normally, this catalyst was reduced by expensive and hazardous liquid reductant. Now, it can be reduced simply by argon plasmas. Since the plasma for catalyst reduction can be simply, easily, and safely operated at room temperature with low energy requirements, it has a great potential for extensive applications in chemical syntheses.

During the further investigation on the mechanism for plasma catalyst treatments, we have observed an enhanced interaction between the catalyst and the support. This leads to the formation of a very different metal-support interface. Figures 5c and 5d show a novel interface between Ni and the support (Ta<sub>2</sub>O<sub>5</sub> and ZrO<sub>2</sub>), obtained from the argon plasma treatment [20]. This novel interface is sometimes very important to the semiconductor catalyst. The plasma treatment can readily generate such interface with no complex operation. It is the difference between the treatment methods that results in different interfacial structures. The plasma preparation uses the plasma treatment to replace the drying or calcination thermally. In comparison, the formation of unfavored interfacial region over the conventional catalyst, as listed in Figs. 5a and 5b, is likely due to diffusion caused by the thermal effect of the conventional preparation.

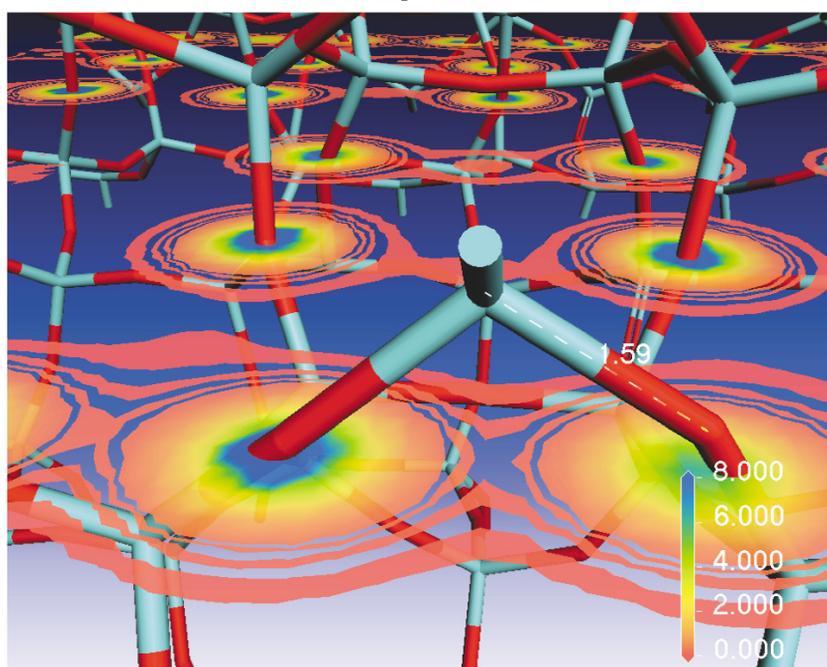


**Fig. 5** Transmission electron microscopy (TEM) images of calcined (a) Ni(NO<sub>3</sub>)<sub>2</sub>/Ta<sub>2</sub>O<sub>5</sub> and (b) Ni(NO<sub>3</sub>)<sub>2</sub>/ZrO<sub>2</sub>, and plasma-treated and -calcined (c) Ni(NO<sub>3</sub>)<sub>2</sub>/Ta<sub>2</sub>O<sub>5</sub> and (d) Ni(NO<sub>3</sub>)<sub>2</sub>/ZrO<sub>2</sub> [20].

In addition to the changes of the surface morphology, the plasma treatment also induces a significant modification in the catalyst acidity as mentioned earlier [22,24,26]. The modified acidity would likely be one of the reasons causing the changes of the interface between the catalyst and the support. The modification mechanism is still not clear. However, we must keep in mind that many active sites on the catalyst surface possess electronic defects. These defects would create a natural intense electric field that could be stronger than any electric field applied for the initiation of man-made plasmas. It provides a solid basis for the approach of using nonthermal plasmas for catalyst treatments or modifications because plasma treatments can greatly alter the electric field of defects on catalyst surfaces, as evidenced by the generation and redistribution of acidic sites on catalysts tested. Another example to demonstrate the importance of electric field on catalysis is with the zeolite catalyst. Figure 6 exhibits a calculated electric-field distribution within the framework of ZSM-5 zeolite. It is known that the framework of zeolites can create a very intense natural electric field, as intense as  $1 \text{ V}/\text{\AA}$ , which is much stronger than any electric field applied for initiation of any man-made plasmas. When these zeolite powders are further charged by external plasmas, the “natural” electric fields within the framework would be modified and, as a result, amazing catalytic reactions would proceed. It is expected that not only the plasma affects the electric fields inside the zeolite pores, but the electric fields of zeolites also affect the gas discharge plasma. Figure 1b presents an unusual glow in the presence of catalyst powder, which demonstrates the effect of electric fields of catalysts on glow discharge plasma. If no catalyst powder is loaded, the glow is uniform without striations at the same condition as shown in Fig. 1a. Our experimental result shows that porous materials such as zeolite and alumina can easily initiate such striations. For nonporous materials, such as TiO<sub>2</sub> and ZrO<sub>2</sub>, these phenomena are still present but at relatively lower pressures. This may indicate an enhanced effect of the electric field within nanopores. We are further investigating the interactions of plasmas with the “natural” electric fields of zeolites and surface



Top view



Side view

**Fig. 6** Calculated electron density distribution of natural electric field within ZSM-5(MFI) zeolite framework (length is in Å and electron density is in  $e/\text{Å}^3$ ). Obtained from a calculation using MS Dmol<sup>3</sup> Module.

defects. The correlation between the modified electric fields of the zeolites or the surface defects by plasmas, and the resulting catalytic product distribution will be reported in our future works.

As speculated, even without man-made plasmas, some catalysts, especially zeolites, would already be in some kind of “natural gas discharge” status. For example, gases in the nanopores could be broken down and nanoscale discharges would be generated, which also might be one of the reasons for the unique activity of zeolites for so many reactions. The only difference between the “natural gas discharge” and the man-made plasmas, we can imagine, is the size of the “gas discharge” region. The man-made plasmas are in macroscale and normally generated by dc or ac high voltages, while the “gas discharge” created by the catalyst defect or by the zeolite framework is in the nanoscale with a high-field character. In addition, there is evidence supporting the postulated analog between the man-made gas discharge plasmas and the environment inside the catalyst pores, such as zeolite catalysts [35]. It is believed that, in order to further improve the performance of gas discharge plasma reactions and to better understand the reactions of either catalysis or plasmas, we should acknowledge the perfect electric field in nature and mimic it in our future design of gas discharge reactors. Typically, almost all the investigated organic chemical syntheses using gas discharges employed high voltage to generate plasmas, no matter what kind of plasmas applied. Many excited species, with relatively lower energies, do not contribute to syntheses but consume much energy and decrease selectivity. As a result, it has dramatically limited the applications of such high-voltage-generated plasmas for effective syntheses of gaseous and liquid organics. The analog between gas discharge plasmas and the environment within the catalyst pores suggests that future development of gas discharge plasma for organic syntheses should shift from the high-voltage plasmas to high-field plasmas. This of course raises some challenges for the plasma design/generation community, but it represents a greater opportunity for the rest of scientific world.

## CONCLUSION

The catalyst preparation with nonthermal plasma treatment leads to a formation of highly dispersed special nanostructured metal cluster, which could lead to a better low-temperature activity, an enhanced stability, and a better anti-carbon deposition performance. The improvement in the catalyst properties with nonthermal plasma-treated catalyst can reduce or avoid the use of chemicals. The metal ions applied can be effectively reduced at room temperature during the nonthermal plasma treatment, which has induced a development of nonthermal plasma reduction of catalysts. The reduction using hydrogen at high temperatures or using hazardous chemicals can be replaced by the developed plasma reduction. Further development in catalyst preparation with nonthermal plasma treatment is leading to practical applications for organic syntheses sooner than direct plasma conversion.

An analog between the man-made gas discharge plasmas and the environment inside the zeolite pores and around surface defects is proposed. The analog suggests a shift from high-voltage to high-field plasma for future development of organic syntheses using discharge plasmas. It is believed that in order to further improve the performance of gas discharge plasma reactions and to better understand the reactions of either catalysis or plasmas, we should further investigate and mimic the perfect electric fields in nature.

## ACKNOWLEDGMENTS

The support from the National Natural Science Foundation (under contract 20225618 and 20490200), SINOPEC (under contract X501031), 973 project (under contract 2005CB221406), and the Program for Changjiang Scholars and Innovative Research Team from the Ministry of Education of China is greatly appreciated. Partial support from Welch Foundation and the Organized Research Grant at Texas A&M University-Commerce is acknowledged.

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