Reforming glycerol under electro-statically charged surface conditions

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Catalysis is dependent on electronic interactions that occur between substrate molecules and surface atoms of a catalyst. Although these electronic interactions have been altered by means of adding dopants, the effect of direct extraneous alteration of electronic structure of catalyst-substrate system has not yet been studied. Here, we studied the effects of electrically charging a conductive catalyst surface (Ni–Ce/carbon) and a substrate system (glycerol nanodroplets) on the efficacy of steam reforming. The behavior of the system when the catalysts surface was excited with electrons while the substrates were positively charged was studied at varying temperatures and polarity. It was evident that throughout the temperature ranges tested, the hydrogen yields increased consistently when the system was charged as opposed to reforming under neutral conditions. Reforming under electrically charged surface conditions resulted in a 25% increase in hydrogen selectivity, and 64% increase in substrate conversion. The effects were more pronounced at temperatures below the glycerol boiling point. These results expose the possibility of controlling the outcome of a reaction by extraneous manipulation of the electronic structure of a catalyst/substrate surface.

Introduction

Ever increasing demand for energy coupled with inevitable depletion of fossil fuels has impelled the research community to search for alternate energy sources. Hydrogen is widely considered as one of the most promising alternate energy sources mainly in the context of providing mobile power.[1,2] Hydrogen is beneficial because the byproducts of hydrogen-to-energy conversion are generally benign for human health and the environment.[1]

At present, there are several hydrogen generation techniques under various stages of development that include gasification, partial oxidation, aqueous phase reforming and steam reforming. Among these, steam reforming of oxygenated hydrocarbons is the most widely used when the substrates are in liquid phase/vapor phase.[1,3,4] Steam reforming uses high temperature low pressure conditions to reform substrates in the gas-phase while aqueous phase reforming is carried out at liquid-phase under relatively lower temperatures and higher pressures. Aqueous phase reforming (APR) is a more recent concept and is still under research and development.[5–8] Gasification is presently limited to solid substrates.

Although steam reforming is the most widely used method to produce hydrogen, this method is unable to handle most bio-renewable substrates such as lipids, carbohydrates and their derivatives that are highly viscous.[1,4,9–12] APR, on the other hand, allows processing of viscous feedstock that cannot be vaporized without decomposition. While steam reforming is conducted at high temperatures and atmospheric pressure, APR is carried out at lower temperatures and comparatively much higher pressures.[8,13,14] Consequently, the practical applicability of APR is still limited. Lower temperatures do not favor thermodynamics since the reforming reaction is endothermic and is also kinetically hindered. Apparently, according to the *Le Chatelier-Braun principle*, higher partial pressures of the H_2 product do not board well for the reaction as well. This research attempts the development of a technique that could overcome the limitations of both these techniques, *i.e.*, steam reforming and APR, when reforming highly viscous oxygenates.

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Broader context

This study attempts to increase the reaction rates associated with aqueous phase reforming (APR) by exerting the necessary activation energy *via* direct electron manipulation. By increasing the electron density of the catalyst surface and the opposite charge density on the substrate droplet surface, we were able to prove that hydrogen and oxides of carbon yields/selectivity could be significantly enhanced. These observations were pronounced especially at temperatures below glycerol boiling point – where a majority of this substrate would be in aqueous phase.

The results obtained so far lead us to believe that it may be possible to control the outcome of a catalytic reaction by direct extraneous manipulation of the electronic structure of a heterogeneous catalyst/substrate interface. Results hint that there may be untapped resources at the interface of electrochemistry and traditional catalysis fields which may one day be used to control catalyst selectivity. This is significant since controlling the selectivity of a catalyst toward desired product(s) is one of the greatest challenges we face in chemistry and chemical engineering.

Electro splitting is a technique that was established in 1917[15] that can be used to atomize a liquid stream by means of electrical force. Here, the liquid is subjected to high electrical potential while it travels through a capillary tube. The electric field forces the liquid to disperse into fine droplets when it comes out from the capillary column.[16–18] Consequently, electro splitting produces a droplet distribution that ranges from micro to nano scale depending on applied electrical field, distance between the electrodes, liquid flow rate and fluid viscosity.[18–20] It is reported that the resulting nano scale spray of droplets have properties of vapor as well as liquid.[16]

The objective of this study was to determine the efficacy of reforming a nanospray of aqueous glycerol and compare it with steam reforming and aqueous phase reforming. Here, the experiments were conducted at different temperatures (250, 275, 300, 325, 350, 400 °C) and six different voltages (0, 2000, 4000, 6000, 8000, 10000 V). Initially, the experiments were conducted at the aforementioned six temperatures while applying no voltage (0 V) and 6000 volts. During the second phase, the experiments were carried out at 6 voltage values at the temperature that was resulted in the best reforming performance (from the first study). The reason for selecting glycerol was because it is a low-value byproduct of the biodiesel production process and it is viscous with a viscosity of 1.5 Pa.s [2]. It was hypothesized that electrically charged electrosplit glycerol droplets will have a higher H_2 selectivity than reforming electrically neutral glycerol droplets/vapor.

Materials and methods

Purified glycerol was purchased from Sigma Aldrich (St. Louis, MO, USA). For the catalyst preparation, the precursors cerium nitrate hexahydrate $[Ce(NO_3)_3.6H_2O]$ and nickel nitrate hexahydrate $[Ni(NO_3)_2.6H_2O]$ were purchased from Sigma-Aldrich (St. Louis, MO, USA). The support material, activated carbon, was purchased from Calgon Carbon Corporation (Pittsburgh, PA, USA). The makeup inert gas used was nitrogen $[N_2]$ (Ultra high purity N_2, Airgas Columbus, MS, USA). The plumbing for liquid flow was based on silicon-coated capillary tubing with an internal diameter of 50μm (Polymicro Technologies Phoenix, AR, USA).

The reaction was carried out in a continuous tubular reactor (quarts tube 1.5 inch diameter), schematic of that depicted in Fig. 1. An aqueous solution of glycerol (glycerol: water molar ratio = 1 : 3) was introduced into the electrospray unit *via* a HPLC (High Pressure Liquid Chromatography) pump (LC-20AT, Shimadzu Scientific Instruments, Columbia, Md., USA) where the liquid flow rate was 0.004 ml/min. The outlet from the electrospray unit was connected to the tubular reactor *via* a capillary line.

The catalyst bed was used as the negative electrode. This was achieved by impregnating the catalyst in a conductive carbon support. Nickel and Cerium oxide were used as the catalyst in this experiment. Catalysts loadings were 10% and 5% for Ni and CeO_2 respectively. Impregnated catalyst was reduced with H_2 gas at 400 °C with 100 ml/min flow rate for 6 h. Finally, the reduced forms of catalysts were calcined at 500 °C for 8 h in N_2.

All the experiments were carried out with a gas hourly space velocity ($G_{Glycerol}HSV$) of 0.35 ml/g-cat/h. The makeup gas flow of 20 ml/min of N_2 was used.

The stoichiometric equation for the glycerol reforming is as follows:

$$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2, (\Delta H°_{298} = +346.4 \text{ kJ/mol})$$
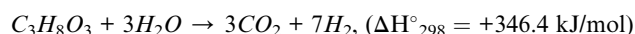
Comparison of gas yields and selectivities were carried out at 6 different temperatures and voltage combinations. First, we tested the hypothesis that "electro spray enhances the aqueous phase reforming" by comparing gas yields and selectivities (H_2, CO, CO_2, and CH_4). The effects of the amount of voltage applied on reformate selectivity was studied in the second phase.

The selectivity and yields for each product was calculated according to the following formula(s):

$$Hydrogen\ Selectivity(\%) = \frac{H_2\ moles\ produced}{Theoretical\ \max imum\ H_2\ moles} \times 100$$

$$Selectivity\ of\ i\ (\%) = \frac{C\ atoms\ in\ species\ i}{C\ atoms\ produced\ in\ gas\ phase} \times 100$$
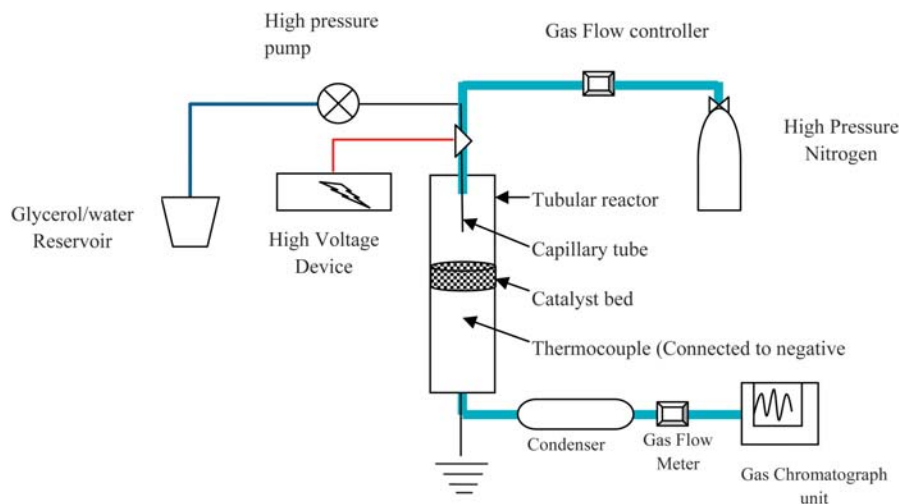

Fig. 1 Schematic of the experimental set-up used for reforming electrically charged substrates on oppositely charged catalyst bed.

Here, the "theoretical maximum H_2 moles" refers to the maximum number of moles of H_2 that can be produced according to reaction stoichiometry.

Results and discussion

The main goal of the first phase of the study was to examine the effects of applied voltage on catalytic reforming of glycerol. In this experiment, the reforming conditions were maintained similar to that of aqueous phase reforming (APR) with the exception of pressure. The reactor was maintained at atmospheric pressure. The experiment was set-up to analyze the four major gaseous compounds produced in steam reforming of oxygenated hydrocarbons, i.e., hydrogen (H_2), carbon dioxide (CO_2), carbon monoxide (CO), and methane (CH_4).[21–26] The reactions were carried out with an applied voltage of 6 kV and neutral conditions while all the other parameters were kept constant. All the data was analyzed statistically with Design Expert software. The comparative yields of selected gases are depicted in Fig. 2.

As depicted in Fig. 2, the yield of H_2 at temperatures below the glycerol boiling point (290 °C) peaked at 250 °C with a yield of 55% and steadily decreased up to the glycerol boiling point. At temperatures beyond the glycerol boiling point, the yield resumed to increase and peaked at 63% at the reaction temperature of 400 °C. The minimum hydrogen yield of 45% was reported at 300 °C. These results are in agreement with aqueous phase reforming (APR) where the highest H_2 yields were observed at 250 °C and 30 bars of pressure.[27–29] However, the interesting observation was that we were able to demonstrate that it is possible to obtain analogous results at atmospheric pressure by imparting the energy for the reaction in the form of electrostatic charges. For comparison purposes previous studies reported that the highest H_2 yields on glycerol steam reforming at 400–850 °C temperature - depending on catalyst, were near 80%.[30–32]

The yields of CO, CO_2 and CH_4 also followed a similar trend, i.e., a sudden reduction of yields at the glycerol liquid-to-vapor transition region. It was evident that methane yield was low

during the entire course of the experiment while carbon monoxide yield decreased in general with increasing temperature. Carbon dioxide yield behaved analogous to hydrogen which is expected since hydrogen and carbon dioxide are the primary products of the steam reforming reaction. The percentage increase in hydrogen yield when charges were applied to the system had maximas of 19.6% at 350 °C and 18% at 275 °C. Also, it was noticed that the effects of charges were more pronounced at lower temperatures. At higher temperatures, it is assumed that the thermal energy exerted to the system far exceeds the minimum amount that is required to overcome the kinetic barrier and thus, the reforming reaction continues effortlessly irrespective of the presence of extra energy in the system in the form of electrical charges.

In order to explain the yield trends more effectively, the selectivity was calculated using yield values. This was done by normalizing the product moles with respect to the maximum stoichiometric yields possible. This was done using carbon balance. The statistical analysis of selectivity data depicts that only H_2 selectivity was significantly affected by temperature, voltage and their interaction. The carbon monoxide and carbon dioxide selectivities were also significantly affected by temperature and voltage but not their interaction. The methane selectivity was not affected by changes in temperature or voltage. The selectivity data are depicted in Fig. 3.

Analogous to what was observed in yield trends, the H_2 selectivity increased when the system was electrically charged. The hydrogen selectivity reached a maximum of 62% when a voltage was applied at a temperature of 400 °C. A minimum selectivity of 40% was observed with an applied voltage at 300 °C - which was closer to the glycerol boiling point. Again, as seen in yield analysis, at temperatures lower than the glycerol boiling point, a spike of hydrogen gas selectivity was observed. The sudden drop of selectivity at 290 °C could be attributed to the energy penalty (energy that is consumed) for latent heat of vaporization of glycerol.

The percentage increase of hydrogen selectivity when the system was charged as compared to an electrically neutral system
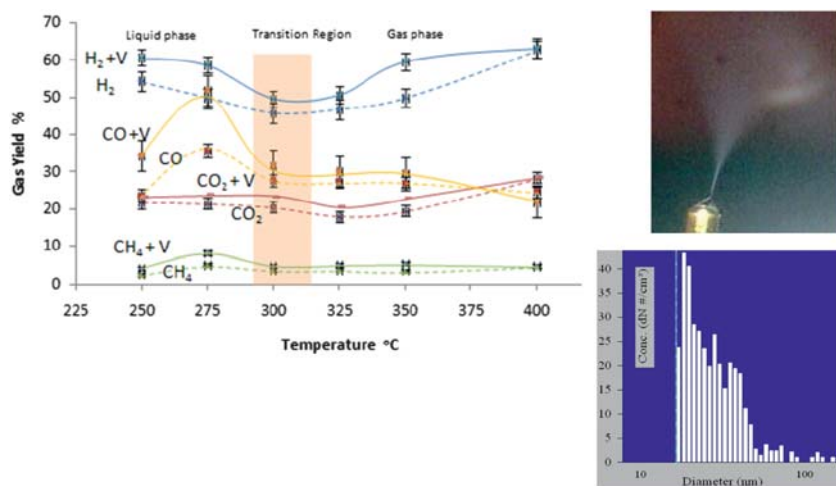

Fig. 2 Reformate composition of neutral (H_2) and electrically charged (H_2 + V) glycerol nanodroplets (mean 50 nm) generated via elctrospraying. Top right figure depicts a charged aqueous glycerol cloud. Bottom right figure depicts the particle size distribution. Particle sizing obtained by Scanning Mobility Particle Sizer (TSI Inc.).
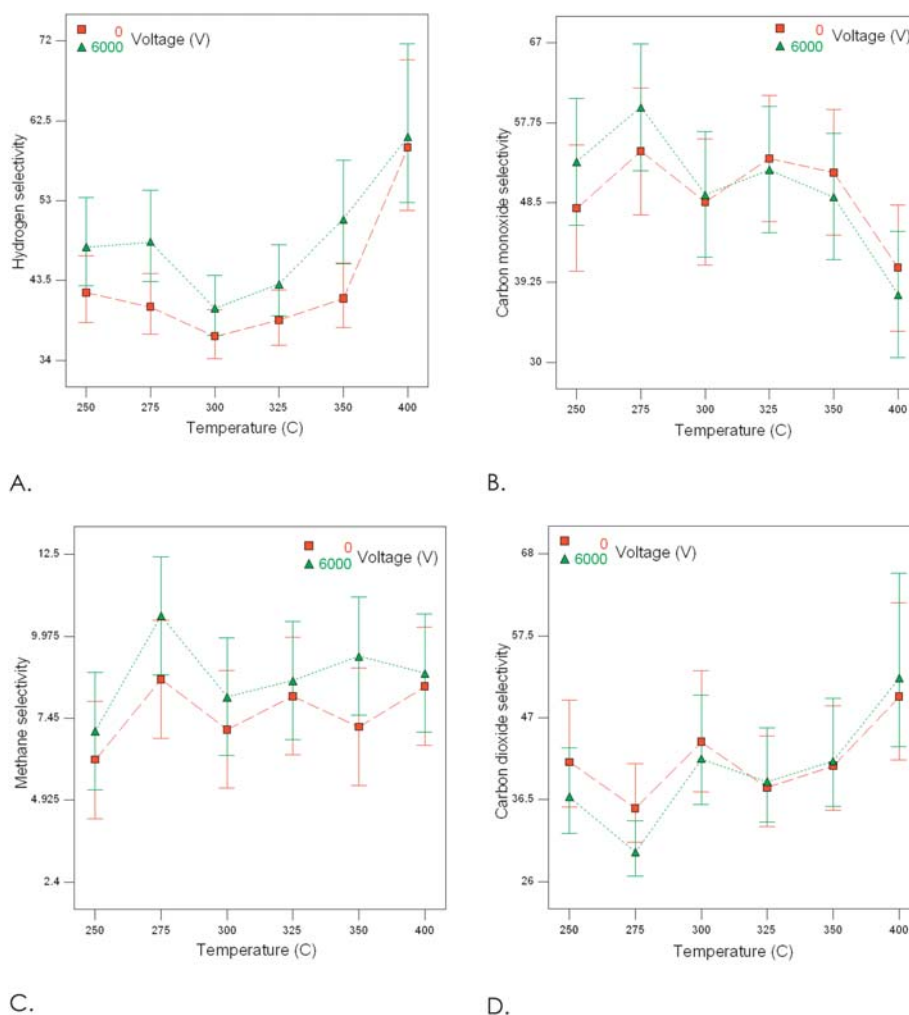
Fig. 3 Gas selectivity variations with temperature in the presence or absence of surface charges.

was highest at 25% at 350 °C, while the lowest was 3% at 400 °C. This observation confirms that the effect of surface charges on the efficacy of reforming diminishes at higher temperatures when all the substrates are in gas-phase.

The selectivity values of other gases also increased when the system was electrically charged, with the exception of carbon monoxide. Carbon monoxide had maximum selectivity of 59% at 275 °C and minimum of 37.8% at 400 °C. The low CO selectivity at 400 °C is expected and correlates well with the high hydrogen yields at this temperature. This observation confirms that the water gas shift reaction, which is an integrated reaction within steam reforming phenomena, occurs as expected, resulting in high hydrogen and carbon dioxide gas yields. Ideally, if steam reforming was the only reaction that occurred, carbon dioxide yields and selectivities should closely correlate to hydrogen gas yields and selectivities. In fact we clearly see this in Fig. 2 and 3.

An idea about the performance of the collective system was obtained by analyzing the substrate (glycerol) conversion and is depicted in Fig. 4. The factorial statistical model showed that the applied voltage significantly affected glycerol conversion at 95% confident level. The glycerol conversion increased clearly when the system was electrically energized as opposed to when the system was operating at an electrically neutral state. The highest

glycerol conversion of 32.7% occurred at 400 °C while the system was charged.

An interesting outcome is the 64% increase in glycerol conversion at 350 °C between charged and neutral substrate reforming. This significant increase in glycerol conversion when the substrate was in aqueous nano-phase correlates well with yield and selectivity spikes of hydrogen, carbon monoxide, and methane just below the boiling point of glycerol.

It was observed that methane selectivity increased with an applied voltage. However, this was not significant when compared to the increases of selectivities of the rest of the reformate gases. An interesting fact was that an increase in negative charges to the catalyst surface had a positive effect on methane selectivity while the substrates were in liquid phase. However, from Fig. 3 it is evident that as the reforming temperature increased beyond the glycerol boiling point, the extraneous charges had insignificant effect on the methanation reaction.

We feel that these quite peculiar observations were a result of a combination of physical and quantum chemical phenomena. The physical phenomena is the simple attraction of the positively charged substrates to the negatively charged catalyst surface that supplemented the Van der Waal's interactions and ultimately
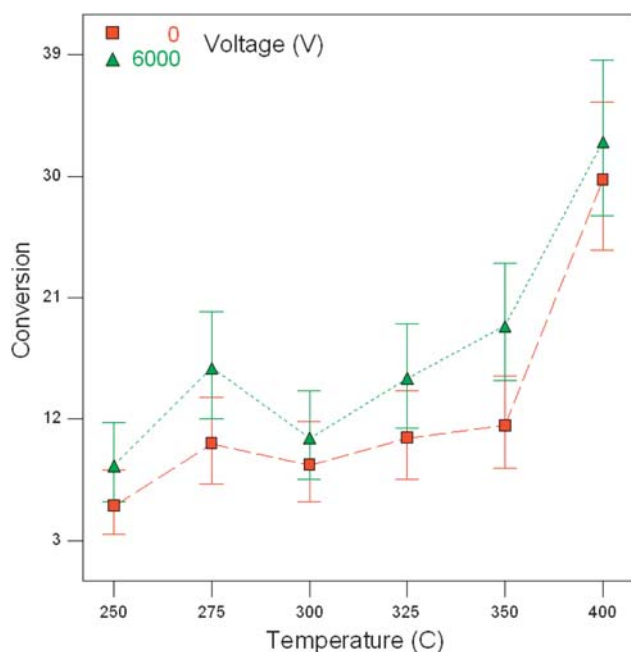
Fig. 4 Glycerol conversion *vs.* temperature – comparison with and without high voltage.

causes adsorption of glycerol and water molecules onto the nickel surface. The chemical phenomena may be a direct result of enhanced chemisorptions followed by d-band broadening due to forced electron saturation in the catalyst surface.

It should be noted that regardless of the phase (gas/liquid), the amount of electrical charges exerted to the liquid stream per unit time was constant. Consequently, the total number of charges per agglomerated droplet will be higher in nano-droplets than bulk liquid phase droplets. On the other hand, it is also noteworthy that the smaller the droplet size, the larger the number of charges carried by a unit volume.[33,34] As an example, it has been estimated that electrosprays consisting of 100 nm diameter methanol droplets can carry 40 times more charges than 1 μm drops of the same volume.[34] Typically, electrospray nanodroplets can carry 50–70% charges of Rayleigh maximum (390 C/ liter).[34,35] Exertion of charges onto aqueous glycerol results in nanodroplets while neutral glycerol results in much larger macro droplets. The increased surface area-to-volume ratio of charged glycerol nanodroplets may have resulted in more favorable conditions for physical attraction of substrates to the catalyst surface as well as enhanced reaction kinetics. Collectively, this phenomenon has translated to consistently increased substrate conversion and reformates gas yields when charged glycerol was used. Additionally, the generally higher reformate yields/selectivities along with higher glycerol conversion levels of vapor phase (>300 °C) substrates in comparison to nano-phase reformates explain this phenomena well.

The chemical phenomena could be directly linked to chemisorption. Chemisorption occurs when chemical moieties form a chemical bond with the surface upon adsorption. Consider two well separated atoms, one that belongs to the substrate glycerol and the other to nickel catalyst, brought closer together. The wave functions of the two atoms start to overlap and form

combinations that describe the chemical bonding of these atoms to form an intermediate adsorbate molecule. Two energy levels exist for the newly adsorbed molecule where the electron can reside; one bonding and one antibonding. According to molecular orbital theory, the stability of the adsorbed molecules depends on the number of electrons occupying bonding orbitals compared with the number of electrons in the antibonding orbitals as well as the degree of interaction and overlap between the two atoms. By increasing the number of electrons on the metal catalyst surface and reducing the number of electrons of the substrate surface in an equal amount, it appears that we have forced the bonding phenomena to dominate over antibonding.

Solid state theory coupled with the Newns-Anderson approximation can be used to further explain what may occur when a molecule approaches a metal surface.[36–38] All metals, including nickel have extended outer *s* or p orbitals, which ensure large electron gas overlap. When metal atoms start coming closer together, the splitting between the bonding and antibonding level increases by increasing the overlap. Eventually, when a high number of orbitals are added, a continuum band is formed. If there is little overlap between the electrons, the interaction is weak and the band is narrow. Such is the case for d-orbitals which have pronounced shapes and orientations that are largely retained in the metal. Hence the overlap between the individual d-orbitals of the atoms is much smaller than of the outer s and p electrons. The latter are strongly delocalized, *i.e.*, not restricted to specific atoms. As a result, they form an almost free electron gas that spreads out over the entire metal. Hence, the atomic *sp* electron wave functions overlap to a great extent, and consequently, the band they form is much broader.

So, what could occur when a glycerol molecule approaches the solid catalyst surface? First, the incoming neutral molecule encounters the weak Van der Waals interaction. As described earlier, the opposite charge attraction bring the molecules closer together and the molecules lose energy upon interaction with the surface and become physisorbed on the surface. When the physisorbed molecule is moved closer to the surface, it will feel a strong repulsion and gain energy. However, the molecule responds by changing its electron structure during the interaction with the surface and dissociates into two or more chemisorbed moieties. In the neutral state, we see that this dissociation happens while forming some H_2, CO, CH_4 and CO_2 gases but at a more modest rate. However, when the surface was charged negatively (depending on the amount of potential exerted) the electron density of the transition metal (Ni) increased dramatically while the electron density of the substrate was reduced by a similar amount. Just by analyzing the results (marked increase of reformate yields), we could conjecture that the forced charge saturation induced not only *sp* band broadening but also d-orbital broadening that in turn facilitated substrate adsorption. The induced opposite (positive) charges of the substrate droplets may have subdued the antibonding effects of the outermost *sp* band of the catalyst metal atoms. As soon as the substrate chemisorbed, the system internally rearranged - producing H_2, CO, CH_4 and CO_2 gases while neutralizing and minimizing energy according to thermodynamic/kinetic preferences.

During a second phase, the effects of varied voltage on the efficacy of reforming were evaluated. The experiments were conducted between 0–10kV at 2kV intervals at a constant
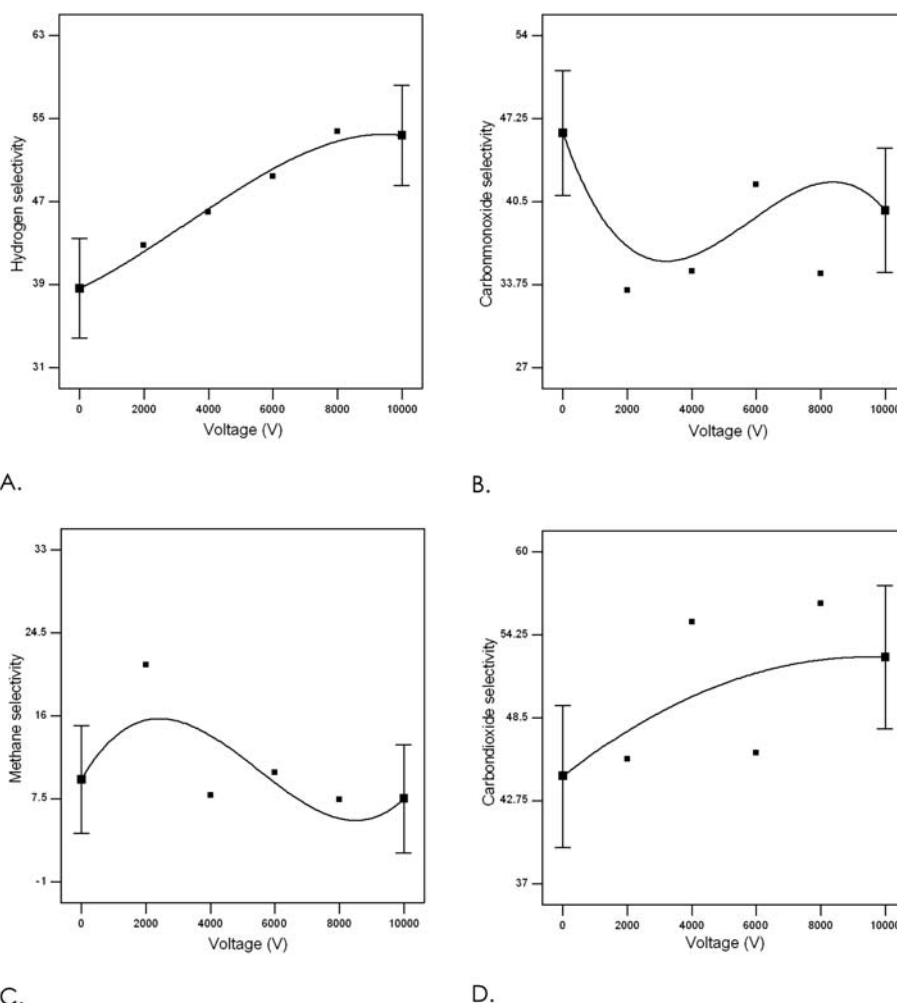
Fig. 5 Effect of voltage on reformate gas selectivity at 350 °C.

temperature of 350 °C. Fig. 5 depicts the variation of reformate gas selectivities with voltage. The statistical model predicted that only H_2 and CO_2 were significantly affected by voltage. This is an interesting result since H_2 and CO_2 are the two major final products of steam reforming. It is clear that increasing voltage had a proportionately positive impact on hydrogen yields. A maximum hydrogen yield of 62% was observed at 8 kV while a minimum of 46% was observed under neutral conditions. At 8 kV, a 40% increase in hydrogen selectivity was observed as compared to that of neutral glycerol reforming. This is a strong indicator that electrical charges favor reforming. The CO_2 and CO selectivities oscillated with increasing voltage in an almost identically opposing manner, *i.e.*, CO_2 selectivity peaks super-imposed with CO selectivity minimums. The general trend of carbon dioxide selectivity was incremental and this is in agreement with the general increase in hydrogen selectivity that was observed with increasing voltages. A maximum of 53% of H_2 selectivity at 350 °C was obtained at 8000 V and 10000 V. It was evident that methane yield reduced with increasing voltage. The observations suggest that increasing voltage favored reforming and water gas shift reactions while disfavoring methanation.

It is interesting to note that the benefits of reforming with electrically charged catalyst/substrate system was pronounced only up to a certain charge level. For example, the effects of charges peaked around 8 kV for the Ni/glycerol system we studied. This essentially suggests that the response of a catalyst/substrate system to increasing density of electrons may be material dependant and opens up an exciting area for further exploration.

Conclusions

Studies were conducted to ascertain the effects of electrically charging a catalyst surface and a substrate system on steam reforming. First, the response of the system when Ni/carbon was negatively charged and aqueous glycerol nanodroplets were positively charged was studied at varying temperatures. It was evident that throughout the temperature ranges tested, the H_2 yields increased when the system was charged as opposed to reforming under the neutral conditions. Specifically, it was noted that reforming with electrically charged surfaces resulted in a 25% increase in hydrogen selectivity, and 64% increase in glycerol conversion. The beneficial effects of electrically charged reforming were pronounced at temperatures below the glycerol boiling point and diminished as the temperature increased in the vapor region. A significant drop in reformate gas

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yields/selectivities was observed at temperatures neighboring the glycerol boiling point and it is attributed to energy penalty for latent heat of vaporization. Increasing the voltage up to 8 kV had a positive impact on reformate yields. However, increasing voltages beyond this point had insignificant impact on the system performance. Although further studies are needed to verify, it is surmised that the benefits of extraneous charge alteration may be due to enhanced physical (transport phenomena and phys-isorption) and chemical (chemisorption) phenomena that occur between the catalyst surface and the substrate(s). This is an exciting observation and we expose the likely possibility of controlling the outcome of a reaction by extraneous tuning the electronic structure of a catalyst/substrate surface.

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