

Article

Tribo-Catalytic Conversions of H₂O and CO₂ by NiO Particles in Reactors with Plastic and Metallic Coatings

Hua Lei ¹, Xuchao Jia ¹, Hongbo Wang ¹, Xiaodong Cui ¹, Yanmin Jia ² , Linfeng Fei ³ and Wanping Chen ^{1,*}¹ School of Physics and Technology, Wuhan University, Wuhan 430072, China² School of Science, Xi'an University of Posts and Telecommunications, Xi'an 710061, China³ School of Physics and Materials Science, Nanchang University, Nanchang 330031, China

* Correspondence: wpchen@whu.edu.cn

Abstract: NiO has been found to be highly outstanding in producing H₂ and O₂ from H₂O through magnetic stirring, while its capability for the reduction of CO₂ through mechanical stimulation has not been investigated. Presently, NiO particles have been employed to promote the conversion of H₂O and CO₂ enclosed in reactors into flammable gases through magnetic stirring. For a 150 mL glass reactor filled with 50 mL water, 1.00 g of NiO particles, and 1 atm of CO₂, 24 h of magnetic stirring using a home-made Teflon magnetic rotary disk resulted in the formation of 33.80 ppm CO, 10.10 ppm CH₄, and 12,868.80 ppm H₂. More importantly, the reduction of CO₂ was found to be substantially enhanced through coating some polymers and metals on the reactor bottoms, including 25.64 ppm CO and 70.97 ppm CH₄ obtained for a PVC-coated reactor and 30.68 ppm CO, 52.78 ppm CH₄, 3.82 ppm C₂H₆, and 2.18 ppm C₂H₄ obtained for a stainless steel-coated reactor. Hydroxyl radicals were detected using fluorescence spectroscopy for NiO particles under magnetic stirring in water. A tribo-catalytic mechanism has been proposed for the conversion of H₂O and CO₂ into flammable gases by NiO particles under magnetic stirring that is based on the excitation of electron-hole pairs in NiO by mechanical energy absorbed through friction. These findings not only reveal a great potential for mechanical energy to be utilized for CO₂ conversion but are also valuable for fundamental studies.



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1. Introduction

As one of the most abundant clean energies in ambient environments, mechanical energy is receiving more and more attention to be harvested for chemical reactions [1–8]. In research, piezoelectric materials are mechanically stimulated to deform with voltages generated across them, which have been demonstrated useful for water splitting [9–13], organic pollutant degradation [14–18], tooth whitening [19], and tumor therapy [20–22]. The piezoelectricity of the materials employed plays a vital role in the conversion of mechanical energy to chemical energy in these utilizations, and this type of energy conversion has been widely termed as piezo-catalysis and is confined to piezoelectric materials only. As a result, technologies suitable for both piezoelectric and non-piezoelectric materials to harvest mechanical energy have been intensively pursued [4]. It is well known that mechanical energy can be readily absorbed by materials through friction and converted into other forms of energy, including chemical energy, heat, and light [23]. As a matter of fact, a concept for the conversion of mechanical energy to chemical energy by materials through friction, namely tribo-catalysis, had been proposed several decades before [24]. However, there had been no common, specific applications for tribo-catalysis for a long period of time [25]. In 2019, Li et al. first reported tribo-catalytic degradation of organic pollutants by Ba_{0.75}Sr_{0.25}TiO₃ nanoparticles [1]. Additionally, in the following couple of years, tribo-catalytic degradation of organic pollutants has already been investigated for many

other materials, including both piezoelectric and non-piezoelectric ones [2,3,5,6,26,27]. It is particularly interesting that tribo-catalytic reduction of CO₂ has very recently been revealed for TiO₂ nanoparticles [28,29], which demonstrates a direct utilization of mechanical energy for CO₂ conversion. Obviously, tribo-catalysis must have been strangely neglected for decades, and many more investigations are highly desirable to fully explore its potential in harvesting mechanical energy from ambient environments.

It should be pointed out that Cu₂O and some other metal oxides had been investigated with regards to their capability to split water through magnetic stirring by Domen et al. in 1998 [30], in which the mechanical energy supplied by magnetic stirring was proposed to be converted to chemical energy of H₂ and O₂ with Cu₂O functioning as a mediator or catalyst. This was the first time that the concept of mechano-catalysis was proposed. Subsequently, it was discovered that NiO performed outstandingly among dozens of metal oxides in the production of both H₂ and O₂ [31]. A mechanism based on redox reactions between metals and metal oxides has been proposed for the formation of H₂ and O₂ from H₂O by metal oxides under magnetic stirring [32]. This mechanism is quite different from tribo-catalysis and the implications of Domen et al.'s findings for tribo-catalysis have been quite neglected. With all these recent findings for tribo-catalysis, it is meaningful to carefully investigate the capability of NiO and other metal oxides for the conversion of H₂O and CO₂ as well through friction. Currently, we have conducted such an investigation for NiO and obtained some highly interesting results. Through magnetic stirring, NiO particles are found to be able to convert H₂O and CO₂ enclosed in reactors into flammable gases of CO, CH₄, and H₂, among which H₂ has an especially high concentration. More interestingly, some plastics and metals have been coated separately on the reactor bottoms to form friction with NiO particles in magnetic stirring, and the concentrations of CO and CH₄ are found to have substantially increased. These results should be highly important for tribo-catalysis, both fundamentally and practically.

2. Materials and Methods

2.1. Fabrication of Teflon Magnetic Rotary Disks

To ensure as many NiO particles as possible form friction with reactor bottoms during magnetic stirring, Teflon magnetic rotary disks were designed and fabricated. As shown in Figure 1, a cross-shaped groove (4 mm wide × 2 mm deep) formed on one major surface of a Teflon disk (φ 35 mm × 5 mm), and 18 magnets (φ 5 mm × 5 mm) assembled and mounted on the other surface of the disk, which was then encapsulated by epoxy. With the groove facing downward, such a Teflon magnetic rotary disk can be driven to rotate in a reactor through an ordinary magnetic stirrer, and NiO particles are able to enter the interface between the disk and the reactor bottom through the groove.



Figure 1. Photographs of a home-made Teflon magnetic rotary disk, back side and front side, separately.

2.2. Forming Plastic and Metallic Coatings on the Bottoms of Quartz Glass Reactors

Some commercial quartz glass reactors of φ 50 mm × 75 mm (150 mL) were used directly, while others were first modified through coating plastic and metallic disks of

ϕ 49 mm \times 1 mm separately on their bottoms. In this way, reactors with different bottoms of glass, plastics, and metals were obtained separately and could be used for comparison.

2.3. Materials Characterizations

The crystal structure of NiO powders investigated in this study was measured by X-ray diffraction (XRD, SmartLab SE, Rigaku, Japan) with Cu K α radiation. The morphology and microstructure of the NiO powders were observed by a scanning electron microscope (SEM, Zeiss GeminiSEM 500, Oberkochen, Germany).

2.4. Tribo-Catalytic Activity Measurement

In a typical experiment, 1.00 g of NiO particles, 50 mL of deionized water, and a Teflon magnetic rotary disk were placed separately in a reactor. It is worthy to note that in initial investigations by Domen et al. on splitting water by NiO particles under magnetic stirring, only 0.1 g of NiO particles were dispersed in 200 mL of deionized water [30,31]. During our series of tribo-catalysis studies, we discovered that using a much larger amount of tribo-catalyst relative to deionized water can substantially improve tribo-catalytic efficiency [1,27–29]. CO₂ gas (99.99%) was bubbled through the water for 1 h to remove air, at which point the reactor was gas-tight. The Teflon magnetic rotary disk was driven to rotate at 400 rpm through a magnetic stirrer (Chijiu 84-1, Shanghai, China) outside. The reactor was kept in darkness, and the ambient temperature was kept at 25 °C. After some designated times of magnetic stirring, the gaseous products inside the reactor were sampled and analyzed through a gas chromatograph (GC-2014C, Shimadzu, Kyoto, Japan) equipped with a thermal conductivity detector (GC-TCD, Kyoto, Japan) and two flame ionization detectors (GC-FID1, GC-FID2, Kyoto, Japan). However, the oxygen content of the gaseous products cannot be measured using this method.

There were many configurations for H₂O and CO₂ enclosed in the reactors to be converted through magnetic stirring in this study. For every configuration, at least three independent experiments were conducted. According to their data obtained through gas chromatograph measurement, one experiment was chosen as representative for the configuration, and its data were adopted.

2.5. Detection of Hydroxyl Radicals

Typically, in a flat-bottomed glass beaker (ϕ 45 mm \times 60 mm), 1.00 g of NiO particles were suspended in 50 mL of a 0.5 mM terephthalic acid (TA) aqueous solution containing 2 mM of NaOH. The mixture was magnetically stirred through a Teflon magnetic rotary disk at a speed of 400 rpm on a magnetic stirrer in the dark at room temperature (25 °C). During the test, 3 mL of solution was taken out at each 2 h interval and centrifuged at 8000 rpm for 5 min to remove NiO powder, and then the fluorescence spectra were measured on a fluorescence luminescence spectrophotometer (FL, Hitachi F4600, Tokyo, Japan) using the 315 nm excitation light. Hydroxyl radicals react with TA to form 2-hydroxyterephthalic acid (TAOH), which has a characteristic photoluminescence signal centered at 425 nm.

3. Results and Discussion

In research by Domen et al. on water splitting by metal oxides under magnetic stirring, some of the metal oxides employed were powders with micrometer-sized grains [30,31]. Additionally, in our study on tribo-catalysis, we have also observed that those powders of interest are not necessarily nanoparticles, which form a sharp contrast with those in photo-catalysis. As a matter of fact, we had compared several kinds of NiO commercial powders and then chose one to be employed in this study, which was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) with a purity of 99.0%. Its XRD pattern and microstructure are shown in Figure 2. As shown in Figure 2a, all the diffraction peaks are seen at 37.2° (111), 43.3° (200), 62.9° (220), 75.4° (311), and 79.4° (222), which match well with the standard diffraction pattern of NiO (JCPDS #47-1049). No obvious impurity peaks were detected, indicating this commercial NiO powder had a high phase purity. The SEM

image (Figure 2b) shows that its NiO particles were quite uneven in size, ranging roughly from 100 nm to 1 μm . Some particles were irregular polyhedrons with distinct edges, which suggested a high crystallinity. A recent paper [33] clearly demonstrated the importance of high crystallinity for tribo-catalysts.

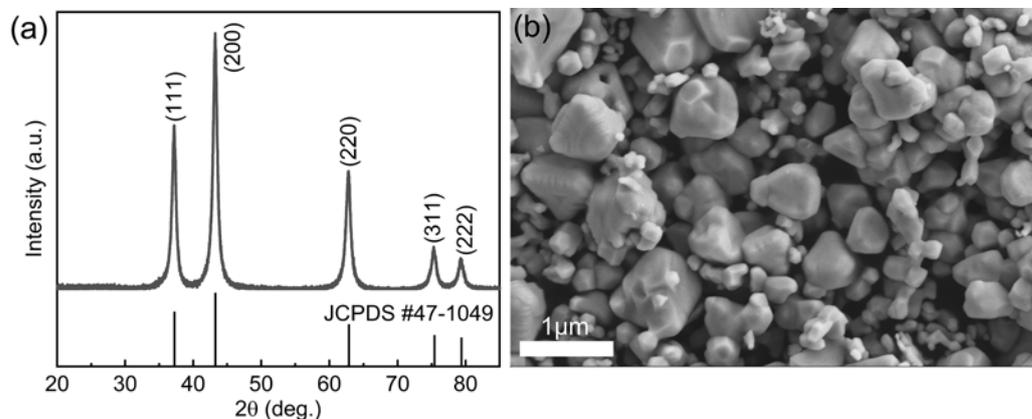


Figure 2. (a) XRD pattern of the commercial NiO powder employed in this study; (b) SEM image of the commercial NiO powder, with NiO particles ranging roughly from 100 nm to 1 μm .

Teflon magnetic stirring rods were not designed for applications in tribo-catalysis. Instead, Teflon magnetic rotary disks have been deliberately designed to form a large interface with beaker/reactor bottoms in magnetic stirring and should be especially suitable for applications in tribo-catalysis [27]. In a previous investigation, greatly enhanced tribo-catalytic degradation of organic pollutants has been observed for TiO₂ nanoparticles, using the well-known commercial photocatalyst P25 when Teflon magnetic rotary disks are adopted in magnetic stirring [27]. Additionally, in this study, we tested first the Teflon magnetic rotary disks we fabricated to drive TiO₂ nanoparticles of P25 to convert H₂O and CO₂ enclosed in reactors to CO, CH₄, and H₂, and some of the results are shown in Figure 3. In a control experiment in which a Teflon magnetic rotary disk was driven to rotate via magnetic stirring in deionized water in a gas-tight reactor, a small quantity of flammable gases (2.10 ppm CH₄, 2.50 ppm CO, and 6.00 ppm H₂) was detected 24 h after magnetic stirring started. While for the experiment with 1.00 g P25 of TiO₂ nanoparticles dispersed in deionized water in a gas-tight reactor, as much as 9.10 ppm of CH₄, 29.00 ppm of CO, and 40.50 ppm of H₂ were produced after 24 h of magnetic stirring. Obviously, the addition of P25 had dramatically promoted the conversion of H₂O and CO₂.

In previous investigations on the tribo-catalytic conversion of H₂O and CO₂ by TiO₂ nanoparticles, four Teflon magnetic stirring rods were employed simultaneously in magnetic stirring to enhance the friction energy absorbed by TiO₂ nanoparticles [28,29]. Though TiO₂ nanoparticles had been found to have a tribo-catalytic effect on the conversion of H₂O and CO₂ to CO, CH₄, and H₂, the efficiency was extremely low. Compared with these results, the Teflon magnetic rotary disks show a clear advantage for applications in tribo-catalytic H₂O and CO₂ conversion. A special experiment had also been conducted in one of these previous investigations [28], in which a home-made glass magnetic stirring rod was used. As no polymers were involved, the formation of CO and CH₄ under this configuration directly demonstrated the tribo-catalytic conversion of H₂O and CO₂.

In evacuated reactors filled with water only, NiO particles have been found to be highly outstanding in the production of H₂ and O₂ through magnetic stirring. Now that the conversion of CO₂ is receiving more and more attention worldwide, it is highly interesting to examine how H₂O and CO₂ enclosed in reactors will be converted by NiO particles through magnetic stirring, and a representative result is also shown in Figure 3. On the one hand, the production of CH₄ and CO by NiO particles is quite similar to that of TiO₂ nanoparticles. On the other hand, the production of H₂ by NiO particles is more than 300 times as much as that for the TiO₂ nanoparticles. In some senses, such a striking

contrast confirms the finding by Domen et al. on the exceptional capability of NiO for the mechanical production of H₂ more than 20 years ago [30,31], which has remained a great challenge to achieve a satisfactory fundamental understanding.

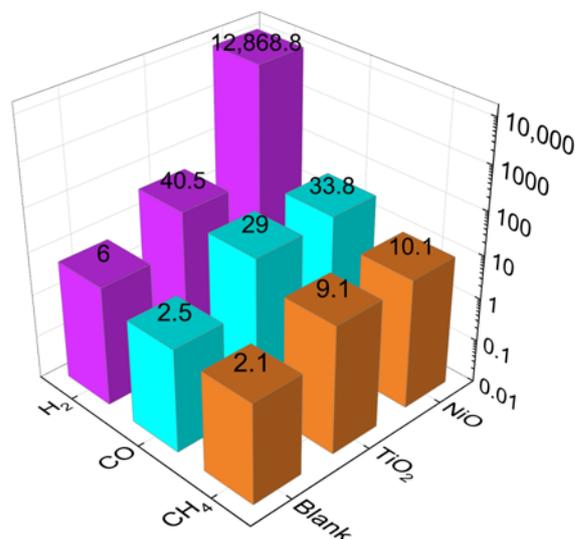


Figure 3. The production of flammable gases from H₂O and CO₂ enclosed in a glass reactor after 24 h of magnetic stirring using a Teflon magnetic rotary disk for three cases: with no particles, with 1.00 g of TiO₂ nanoparticles, and with 1.0 g of NiO particles in the reactor, separately.

Such a large amount of flammable gases observed for NiO particles suggests that NiO will be an important material for the conversion of mechanical energy to chemical energy through friction. It should be pointed out, however, that its amounts of CO and CH₄ are smaller than that of H₂ by more than two orders of magnitude, which indicates that NiO is not so effective for the conversion and recycling of CO₂ through the use of mechanical energy. We have conducted a series of explorations to increase the amounts of CO and CH₄ produced by NiO particles through friction. In one exploration, we modified as-received reactors by coating polymer disks on their bottoms. Such a simple modification greatly affected the amounts and compositions of flammable gases produced by NiO particles through magnetic stirring, as shown by those obtained for PP, PMMA, and PVC-coated reactors in Figure 4. For every reactor, a control experiment was conducted in which no NiO particles were dispersed in the ionized water of the reactor. Perhaps due to the relatively complicated interactions between Teflon and coatings of PMMA and PVC in magnetic stirring [34], relatively large amounts of H₂ were produced in the control experiments with these two reactors. It can be clearly seen that for all three reactors, the addition of NiO particles increased the amount of H₂ by more than 10-fold. More interestingly, for PP and PVC reactors, the total amounts of CO and CH₄ produced by NiO particles were very impressive. Compared with the flammable gases produced by TiO₂ nanoparticles shown in Figure 3, these results suggest that the tribo-catalytic conversion of H₂O and CO₂ by NiO particles can be considerably tailored to yield high productions of both H₂ and C₁ products of CO and CH₄.

Similarly, we have modified some reactors by coating some metallic disks on their bottoms, and the results are also very interesting, as shown in Figure 5. In the control experiments, only small amounts of CO and CH₄ were produced after 24 h of magnetic stirring. In the experiments with the addition of NiO particles, not only were the amounts of CO and CH₄ dramatically increased, but quite large amounts of H₂ were also produced. It should be pointed out that the results obtained for these three reactors are quite different from one another. The amount of H₂ obtained for the Cu-bottomed reactor was much smaller than the other two reactors, and for the stainless steel-bottomed reactor, not only were the amounts of H₂, CO, and CH₄ the highest among these three reactors, but small

quantities of C_2H_6 and C_2H_4 were also observed. Obviously, the friction between NiO particles and these metals influences the conversion of H_2O and CO_2 in a very complicated way. These results further confirm that the tribo-catalytic conversion of H_2O and CO_2 by NiO particles can be greatly tailored, and many more investigations are highly desirable.

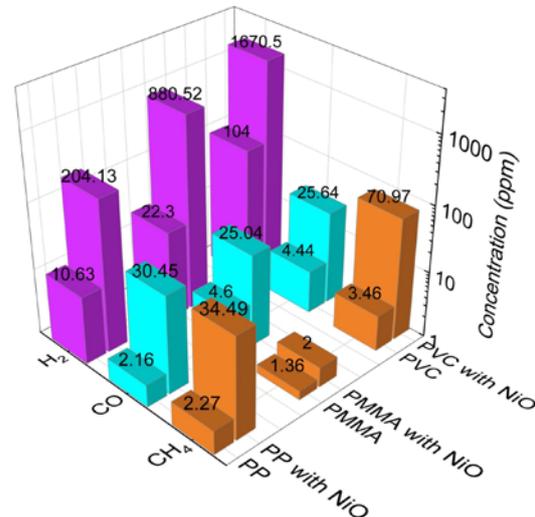


Figure 4. The production of flammable gases after 24 h magnetic stirring for PP, PMMA, and PVC reactors. For every reactor, two experiments were conducted in which no NiO particles and 1.00 g of NiO particles were added to the deionized water, separately.

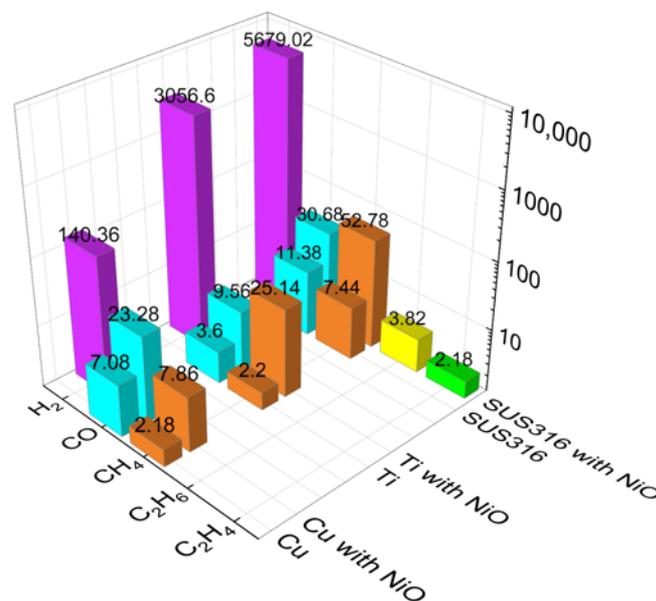


Figure 5. The production of flammable gases after 24 h of magnetic stirring for Cu, Ti, and stainless steel (SUS316) reactors. For every reactor, two experiments were conducted in which no NiO particles and 1.00 g of NiO particles were added to the deionized water, separately.

It should be pointed out that a quite unique back-and-forth conversion between NiO and Ni has been proposed to account for the overall water splitting by magnetic stirring stimulated NiO [32]. Now that tribo-catalysis has been revealed for more and more metal oxides, it is meaningful to carefully investigate the mechanism for the conversion of H_2O and CO_2 by NiO through friction. It is well known that the hydroxyl radical is one of the most reactive radicals for many catalytic reactions in aqueous solutions [35–39]. In this study, we have conducted a routine experiment to detect the formation of hydroxyl radicals for NiO under magnetic stirring in an aqueous solution. For terephthalic acid

suspended with NiO particles, the peak signal of 2-hydroxyterephthalic acid at 425 nm in fluorescence spectroscopy increased steadily with increasing magnetic stirring time, as shown in Figure 6. Meanwhile, 2-hydroxyterephthalic acid was not detected during magnetic stirring in the absence of NiO. As 2-hydroxyterephthalic acid is formed through the reaction between terephthalic acid and hydroxyl, it indicates that hydroxyl radicals are continuously generated in water when NiO particles are kept stimulated through magnetic stirring in water. This result strongly suggests that the conversion of H₂O and CO₂ by NiO under magnetic stirring is realized through the participation of reactive radicals.

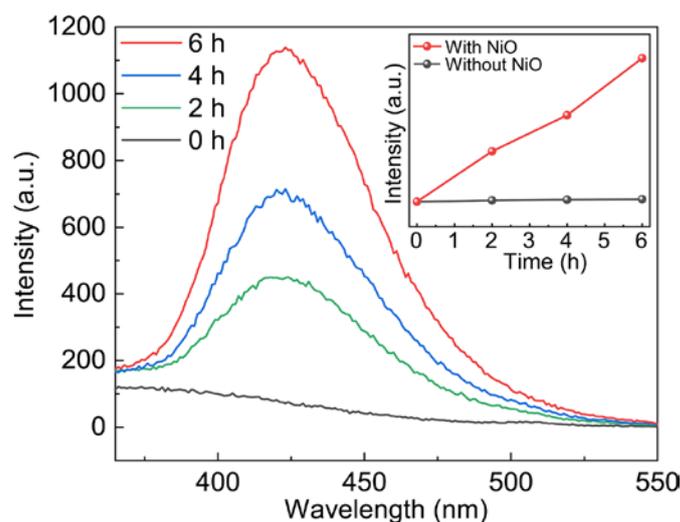
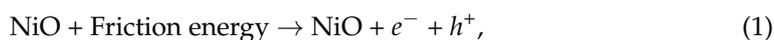


Figure 6. Fluorescence spectra of the 2-hydroxyterephthalic acid solutions taken from a terephthalic acid solution suspended with NiO particles and magnetically stirred (inset: fluorescence intensity of 2-hydroxyterephthalic acid at 425 nm over time).

As a matter of fact, the production of flammable gases by NiO under magnetic stirring is quite similar to that by TiO₂ nanoparticles [28,29], for which a tribo-catalytic mechanism based on the excitation of electron-hole pairs in TiO₂ through mechanical energy has been proposed. With NiO as a typical metal oxide semiconductor, it is reasonable to apply this mechanism for the results in this study, which can be expressed as:



where e^{-} represents an electron excited to the conduction band (CB) and h^{+} represents a hole formed in the valence band (VB).

Once electron-hole pairs are excited in NiO, they are able to produce some reactive radicals in ambient aqueous solutions, including hydroxyl radicals, in the following way:



These radicals are well known for their roles in the degradation of organic pollutants, water splitting, and reduction of CO₂ [1–8,28,29]. Obviously, the conversion of H₂O and CO₂ into flammable gases by NiO particles as a tribo-catalyst can be explained in terms of these radicals, which can be schematically expressed in Figure 7.

This is only a simplified mechanism for the formation of these flammable gases by magnetic stirring stimulated NiO particles, some specific details are still a great challenge to be understood. First of all, it is highly difficult to understand why the coating materials on reactor bottoms have such profound influences on the formation of flammable gases by NiO particles under magnetic stirring, not only on the amount but also on the composition of the flammable gases. Secondly, when NiO particles and TiO₂ nanoparticles are stimulated through magnetic stirring in glass-bottomed reactors, why are they quite similar for the production of CO and CH₄ but greatly different for the production of H₂? As a matter of

fact, Domen et al. had explored this great difference for the production of H_2 among various materials more than 20 years ago, and there has been no satisfactory answer to date [40,41]. Many more investigations are expected to be conducted to achieve an understanding of the singular tribo-catalytic behavior of NiO and to promote the development of tribo-catalysis as a whole.

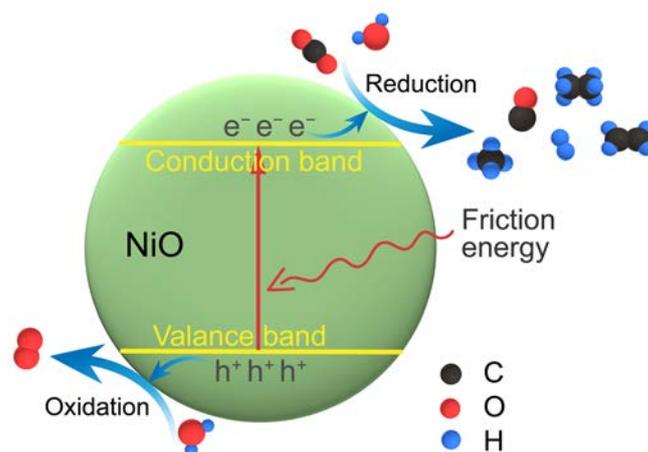


Figure 7. Schematic illustration for the catalytic production of flammable gases by a NiO particle via friction in water.

4. Conclusions

For a commercial glass reactor (150 mL) filled with 50 mL of water, 1.00 g of NiO particles, and 1 atm CO_2 , as much as 33.80 ppm of CO, 10.10 ppm of CH_4 , and 12868.80 ppm of H_2 were produced after 24 h of magnetic stirring using a home-made Teflon magnetic rotary disk. The conversion of H_2O and CO_2 by NiO particles has been further found to be greatly adjustable. The reduction of CO_2 can be dramatically enhanced by coating some polymers and metals on reactor bottoms. As much as 25.64 ppm of CO and 70.97 ppm of CH_4 were obtained for a PVC coating, and 30.68 ppm of CO, 52.78 ppm of CH_4 , 3.82 ppm of C_2H_6 , and 2.18 ppm of C_2H_4 were obtained for a stainless steel coating. Hydroxyl radicals were detected through fluorescence spectroscopy for NiO particles under magnetic stirring, which supports a tribo-catalytic mechanism for the conversion of H_2O and CO_2 into flammable gases by mechanically stimulated NiO particles. The incredible diversity in tribo-catalysis observed among different materials to date not only reveals a great potential for particulate semiconductors to utilize mechanical energy through friction but also presents a great challenge for fundamental research.

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