Molecular Oxygen Promotes Efficient Hydrogen Production from Formaldehyde Solution Using Ag/MgO Nanocatalyst at Room Temperature

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Abstract: We report a highly efficient hydrogen evolution reaction (HER) from formaldehyde/water mixture using MgO supported Ag nanoparticles (AgNPs/MgO) as the catalyst and molecular oxygen as a promoter. The HER rate depends almost linearly on the oxygen partial pressure, and the optimal turnover frequency (TOF) of the silver catalyst exceeds 6,600 h^{-1}. Based on the experimental and theoretical results, a surface stabilized MgO/Ag–•OOH complex is suggested to be the main catalytically active species.

Keywords: Silver, Reforming, Hydrogen.

1. Introduction

Molecular hydrogen (H_2) is of critical importance in the chemical industry and might play vital role in future for benign and secure energy technologies.[1] In early 1990s, a new hydrogen evolution reaction (HER) emerged when chemists investigated the origin of the frequent-occurring detonation during storage of nuclear wastes. It finally led to the conclusion that the combination of water and formaldehyde (HCHO) can be reduced into H_2 gas in highly basic media ($HCHO + H_2O \rightarrow HCOOH + H_2$). A range of heterogeneous catalytic systems were recently developed for HER from alkaline aldehyde solution. However, its practical application is still restricted by several intrinsic limitations, such as the low catalytic efficiency and the use of high concentration soluble bases (e.g., NaOH).[2] More importantly, the fundamental chemical principles responsible for the supported metal nanoparticles mediated HER from HCHO aqueous solution remain unclear. Herein, we report highly efficient H_2 generation from $HCHO/H_2O$ mixture at room temperature using MgO supported AgNPs as an all-solid-state catalyst without any soluble base additives.[3-4]

2. Experimental

Catalytic H_2 production from $HCHO/H_2O$ solution was carried out with 20 mg of catalysts suspended in 5 mL of aqueous HCHO solution (1.0 M) in a 55 mL Pyrex test tube under stirring (400 ± 10 rpm). A water bath was used to maintain the reaction temperature at $25 \pm 0.5\ ^{o}C$ (or $50 \pm 0.5\ ^{o}C$). The oxygen content in the reaction tube was adjusted by bubbling with pure O_2 gas for calculated time, and the tubes were finally sealed with silica gel stoppers. High pressure HER reaction was carried out in a quartz reactor (200 mL) equipped with a steel cap. O_2 pressure was adjusted by an external gas cylinder containing 99.99% O_2. Gas volumes of 400 μL were extracted from the test tubes using a microliter syringe at regular intervals, and GC-TCD was employed for evaluating the gas evolution amount, including H_2, O_2, CO_2 and CO.

3. Results and discussion

AgNPs/MgO nanocatalyst shows an excellent HER activity in $HCHO/H_2O$ solution at room temperature (~25 ^{o}C) and in air ($pO_2 = 0.22$ atm). Figure 1a reveals the steady H_2 evolution from $HCHO/H_2O$ solution (1 M) over 0.8wt % AgNPs/MgO. We find that AgNPs/MgO also effectively catalyzes paraformaldehyde (PF) solution into H_2 under identical reaction conditions. In commercial HCHO solution (i.e., formalin), methanol (MeOH) is pre-added to prohibit the oligomerization of HCHO molecules. Thus it can be inferred that MeOH has no adverse effect on the HER in HCHO solution. On addition of the catalyst into the mixture, constant H_2 gas is immediately generated without any induction period, and no detrimental carbon monoxide is detected during the entire reaction period. The catalyst exhibits high HER activity with TOF = 548 h^{-1} within 6 h reaction (see the Experimental Section for calculation methodology). MgO alone or replacing the support by silica does not show any HER activity, indicating a synergic effect between Ag and MgO.

The most distinctive feature of AgNPs/MgO catalyst is its oxygen-promotion effect (OPE). In the absence of O_2, no H_2 is produced from HCHO solution (Figure 1b). The HER rate is significantly enhanced by increasing p_{O2} from 0 to 1 atm, corresponding to a TOF increase from 0 to 1,969 h^{-1}. Such OPE still works under pressurized conditions. The high-pressure reaction is carried out in a home-made quartz reactor that can stand at most 5 atm. It is found that the HER rate keeps ascending steadily as p_{O2} increases continuously from 1 to 5 atm (Figure 1c). A linear dependency with a slope of 0.85 has been obtained from double logarithmic plots of the initial rate against p_{O2} (Figure 1d), suggesting a quasi-first order kinetics of the HER rate. The TOF value is as high as 6,641 h^{-1} under pressurized condition (5 atm), corresponding to an excellent H_2 production rate of 1,378 L_{H2} h^{-1} $g_{Ag}{}^{-1}$.

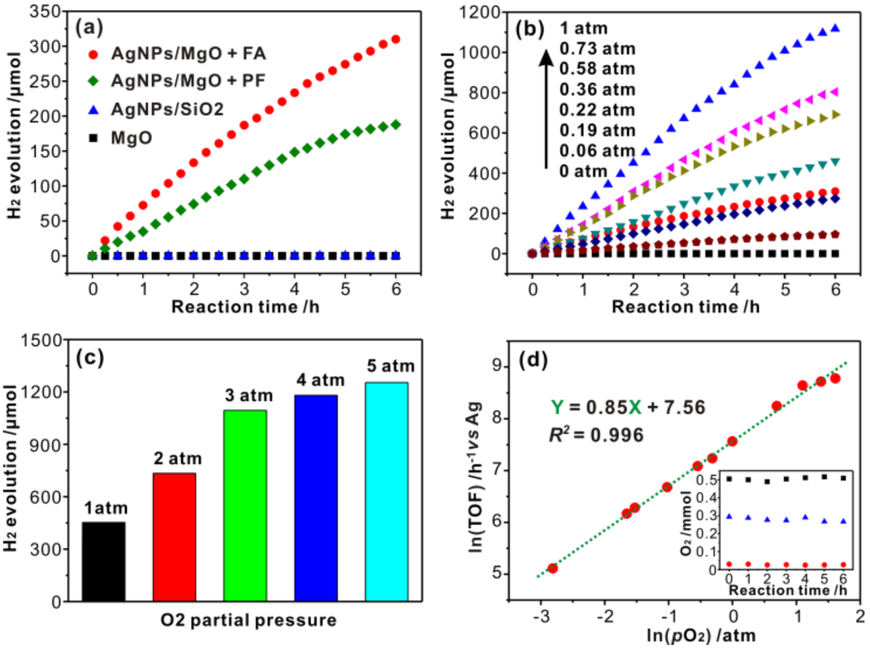

Figure 1. (a) AgNPs/MgO (0.8wt %) catalyzed H_2 evolution from HCHO/H_2O solution (FA, 1 M) or paraformaldehyde solution (PF, ~1 M); the effect of p_{O2} on the HER rate: (b) below 1 atm as a function of reaction time and (c) from 1 to 5 atm within 2 h reaction, and (d) the double logarithmic plots of the initial H_2 evolution rate against pO_2 (inset shows the O_2 content evolution as a function of reaction time).

4. Conclusions

In summary, we show a new and highly efficient HER using AgNPs/MgO as the catalyst and HCHO solution as the substrate at ambient conditions. In contrast to normal HER, we find that molecular O_2 greatly promotes the reaction rate and itself is not consumed during the reaction. We propose that a surface stabilized MgO/Ag–•OOH complex is the catalytically active center that directly participates in the liberation of H_2 as well as the regeneration of O_2 from the reaction system.

References

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