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A Schiff Base Modified Gold Catalyst for Green and Efficient H_2 Production from Formic Acid

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Formic acid (FA) dehydrogenation is an atom-economic way for H_2 production, while diluted FA with extra additive was generally required in heterogeneous dehydrogenation of FA. Here, we report a novel Schiff base functionalized gold catalyst, which showed excellent catalytic performances for H_2 production in catalytic dehydrogenation of high-concentration FA without any additives. The record turnover frequency (TOF) was as high as 4368 h^{-1} in 10 M FA solutions, and was up to 2882 h^{-1} even in 99% FA at mild temperature of 50 °C. According to characterization results, a synergetic mechanism for C-H activation between protonated Schiff base and electronegative gold nanoparticles (NPs) on the interface was suggested to be responsible for its unusual catalytic activity toward H_2 production from FA.

Broader context

Formic acid (FA) is one of the most promising hydrogen carriers for energy storage. However, the evolution of H_2 production from FA dehydrogenation suffers from the limitations of low concentration of FA and the extra additive required, which drastically decrease its hydrogen storage capacity. In this work, we report a previously unappreciated Schiff base modified gold catalyst, which exhibits extraordinarily high activity in concentrated FA solutions without any additives. More importantly, it is the only one which can efficiently achieve H_2 production from pure FA erenow. In addition, a protonated Schiff base was proposed for the first time, in promoting the β-hydride elimination of FA. The unique catalytic feature of gold catalyst towards pure FA dehydrogenation promises a new understanding of gold chemistry. These findings are novel and can be used to guide the rational design of new catalysts for energy storage and evolution by FA.

Formic acid (FA), a natural biomass and also accessible via CO_2 reduction, has attracted tremendous attention as a safe and convenient hydrogen carrier in fuel cells designed for portable use.[1-3] However, efficient heterogeneous catalysis for H_2 production from FA dehydrogenation could only be achieved with the presence of additives, such as triethylamine (NEt_3) and formate, or at a low-concentration of FA (generally less than 1 M),[4,5] which will not only decrease its hydrogen storage capacity, but also restrict its application in fuel cells due to the traces of amines volatilized.[6] Meanwhile, the evolution of FA might also involve the scissor of one of its C-O bond to generate CO and water,[7] which could lower the H_2 production and also lead to the poison of fuel cell catalysts.[8] Therefore, it is highly desired to develop a green and efficient catalyst for H_2 production from FA.

Considering that the base additives contribute to increasing the formate intermediates for further dehydrogenation,[9] a possible way for catalyst design, therefore, was using organic-base groups as proton scavengers, such as amine, to functionalize solid materials to avoid the addition of liquid base. For example, Pd nanocatalysts was recognized as efficient catalysts for the dehydrogenation of aqueous FA only with formate additive.[10-12] Instead, by directly functionalizing amine- over supports to obtain an amine modified Pd catalyst, a comparable activity for FA dehydrogenation can be achieved.[13,14] Different from amine, Schiff base (C=N) is not only a simple base, it also serves as an active group with extensive applications in various homogeneous processes,[15] and metal-Schiff base complexes were reported to show catalytic activity in many reactions such as hydrogenation,[16] Heck Reaction,[17] or even the dehydrogenation of FA.[18] Accordingly, functionalization of Schiff base over supported metal nanocatalysts would provide great opportunity for designing a promising catalyst in the dehydrogenation of FA, while it is a challenge in the heterogenization of Schiff base over support. On the other hand, gold was well-known as a selective catalyst because of its relatively weak activation toward chemical bonds,[19] which was widely used as a promoter to enhance the CO tolerance in FA dehydrogenation,[20,21] however, only a few of Au nanocatalysts

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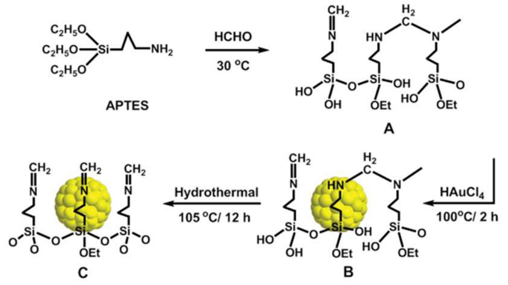
for FA dehydrogenation were reported so far.[9,22,23] In this report, we have successfully synthesized a new type of Schiff base modified gold nanocatalyst by one-pot aldimine condensation and *in situ* reduction of gold precursor. Such Schiff base modified gold catalyst was found to exhibit excellent catalytic performances in the dehydrogenation of high-concentration or even 99% FA, serving as a green and efficient catalyst for H_2 production from FA.

The heterogenizaiton of Schiff base was achieved by one-pot aldimine condensation of (3-aminopropyl)-triethoxysilane (APTES) with formaldehyde. Briefly, a quantitative formaldehyde solution (37%) was added into the APTES aqueous solutions with stirring vigorously at 30 °C, after washing and drying, a precipitation was obtained as a metastable SiO_2 support (Scheme 1A). Next, gold NPs were deposited on the support by reduction of $HAuCl_4$ precursor with metastable aminal on the SiO_2 (Scheme 1B), followed by hydrothermal treatment to obtain the final Schiff base modified gold catalyst (named Au@Schiff-SiO_2, Scheme 1C).



Scheme 1. A synthetic scheme employed for preparing a Schiff base modified gold catalyst.

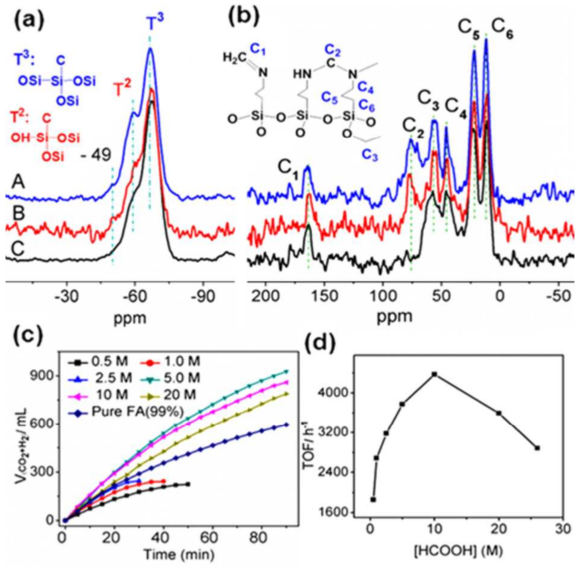


Fig. 1 (a) ^{29}Si CP-MAS NMR and (b) ^{13}C CP-MAS NMR spectra of Samples A, B and C. (c) Decomposition of FA catalyzed by Au@Schiff-SiO_2 at different FA concentrations. Reaction conditions: 5.0 mmol FA or 3 ml reactant solutions (for concentration > 5 M), 30 mg catalyst, 50 ^{o}C. (d) Plot of initial TOF (h^{-1}) versus the FA concentration.

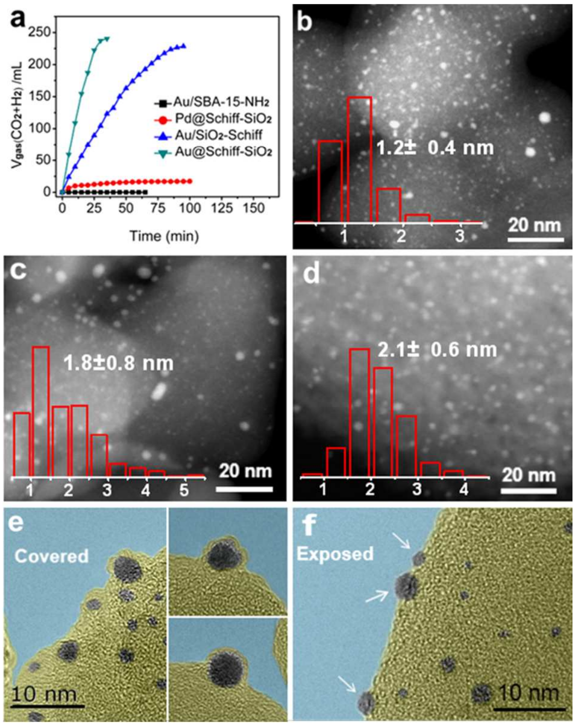


Fig. 2 (a) Decomposition of FA over different catalysts. Reaction conditions: 5.0 mmol (1.5 M) FA, 4.8 μmol metal, 50 ^{o}C. HAADF-STEM images of (b) Au@Schiff-SiO_2, (c) Au/SiO_2-Schiff and (d) Au/SBA-15-NH_2; HR-TEM images of (e) Au@Schiff-SiO_2 and (f) Au/SiO_2-Schiff (uncolored TEM images are present in Fig. S7, ESI†).

^{29}Si CP-MAS NMR and ^{13}C CP-MAS NMR spectra were employed to monitor the evolution of Schiff base during preparation procedures. As shown in ^{29}Si CP-MAS NMR spectra (Fig. 1a), the Si environments of T^2 (-59 ppm), T^3 (-67 ppm) and unhydrolyzed Si-O-C_2H_5 groups (-49 ppm) were distinguished according to NMR chemical shifts, suggesting the hydrolysis and condensation of APTES to SiO_2 solid material with reservation of some alkane-Si moities. For ^{13}C CP-MAS NMR spectra (Fig. 1b), samples A and B exhibited similar resonance peaks of carbon chemical shifts at δ = 164 and 76 ppm, which were attributed to –N=C (C_1) Schiff base and aminal N-C-N (C_2), respectively. While the metastable aminal (C_2) may be further hydrolyzed to -$NHCH_2OH$ and finally be dehydrated to –N=C Schiff base (C_1) during the hydrothermal treatment, as indicated by the peak disappearance at 76 ppm and only the peak at 164 ppm was remained in Sample C. The formed Schiff base was also confirmed by using FT-IR spectroscopy in which a strong peak at 1659 cm^{-1} assigned to the stretch vibration of C=N group of imine was observed (Fig. S1, ESI†).[24] Correspondingly, X-ray photoelectron spectrometry (XPS) results indicated that, the N species of N=C and N-C groups in the Au@Schiff-SiO_2 catalyst was quite different from that of amine (Fig. S2a, ESI†). Due to the strong electron donor capability of the Schiff base, the metallic gold with weak electronegativity was observed on the Au@Schiff-SiO_2 catalyst (83.5 eV, Fig. S2b, ESI†). By comparing the secondary electron

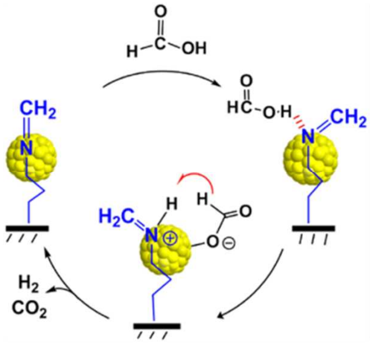
(SE) and backscattered electron (BSE) images (Fig. S3a and b, ESI†), gold NPs with a particle size of ~1.2 nm (Fig. 2b) were found to be half- or full- covered with the moieties of support, which was further confirmed by the HR-TEM images of Au@Schiff-SiO_2 catalyst (Fig. 2e). A statistical analysis of the Au NPs at the edge of SiO_2 showed that 37% of the Au NPs were coated, and the rest were inlaid in the support. Such coating layer might be composed of Schiff base due to the condensation of silicon hydroxyl groups during the hydrothermal treatment.

Subsequently, the catalytic activity of the Au@Schiff-SiO_2 catalyst was tested in a 1.5 M FA solutions without any additives. As shown in Fig. S4a (ESI†), the FA dehydrogenation rate greatly depends on the reaction temperature, and the TOF was up to 2968 h^{-1} at mild temperature of 50 ^{o}C. In addition, the output gas were only H_2 and CO_2, no CO was detected (Fig. S5, ESI†), which serves as “green” gas for fuel cell application. The apparent activation energy (Ea) estimated from the Arrhenius plot was 71.6 ± 1.6 kJ/mol (Fig. S4b, ESI†), which is almost the same as that of the most active homogeneous catalysts.[18] The volume of output gas (CO_2+H_2) versus time at different FA concentrations was shown in Fig. 1c, with the initial TOF shown in Fig. 1d. It was found that there was a volcano relationship between the gas generation rate and FA concentration, that is, the activity increases rapidly as FA concentration up to 10 M, then decreases with the further increasing of FA concentration owing to the decreased water content, which plays an indispensable role in the catalytic dehydrogenation of FA.[25] The initial TOF in a 10 M FA solutions was calculated to be as high as 4368 h^{-1}, which is higher than the reported Pd-based catalysts with additives (Table S3, ESI†). More importantly, even for 99% FA solutions, such gold catalyst also showed very high catalytic activity (TOF up to 2882 h^{-1}). To the best of our knowledge, there was no heterogeneous catalyst being reported for direct catalytic dehydrogenation of pure FA erenow. Despite the theoretical hydrogen content in pure FA is 593 $L_{(H2)}/L_{(FA)}$ (at 273 K), it drops to 22.4 $L_{(H2)}/L_{(FA)}$ in 1 M FA aqueous solutions, and even lower when an additive was present. Hence, the proposed gold catalyst holds great potential in practical application for its excellent catalytic performance on concentrated FA dehydrogenation.

Experimentally, we have also prepared Pd@Schiff-SiO_2 catalyst as that of Au@Schiff-SiO_2 catalyst (Size distribution see Fig. S6, ESI†), however, it exhibited a rather poor H_2 production and was quickly deactivated due to the CO generation over Pd NPs (Fig. 2a and Fig. S14). Meanwhile, by supporting gold NPs on a primary amine-functionalized SBA-15 (Fig. 2d), the decomposition of FA cannot occur (Fig. 2a), in agreement with the previous reports.[5,20,22] It indicated that a synergetic mechanism for FA dehydrogenation between Au and Schiff base promotes its catalytic conversion of FA. Indeed, we have also deposited gold NPs (~1.8 nm) directly on a Schiff base functionalized SiO_2 (Fig. 2c), such Au/SiO_2-Schiff catalyst can also exhibit a desired activity for FA dehydrogenation but with a lower catalytic activity compared to the Au@Schiff-SiO_2 catalyst (Fig. 2a). High-resolution scanning electron microscopy (HR-SEM, Fig. S3b and c, ESI†) and HR-TEM (Fig. 2f) showed that the gold NPs were mainly exposed on the surface of silica support for Au/SiO_2-Schiff. Considering the similar size distribution and electronic property of gold NPs of these two catalysts (Fig. S2b, ESI†), the increased interfacial area between the Schiff base and Au NPs by the formation of encapsulation structure in Au@Schiff-SiO_2 could account for its enhanced catalytic performance.[26]

The influence of Au particle size on the dehydrogenation of FA was studied by altering the Au loading. HAADF-STEM was employed to identify the gold size distribution of the prepared samples (Fig. S8). The three samples with different particle sizes were tested in a 1.5 M FA solutions without any additives at 50 ^{o}C, and their catalytic performance and TOF values were shown in Fig. S9. This result clearly illustrated that the smaller gold nanoparticles exhibit better performance than the larger ones, which is consistent with the previous report.[9]

So far, it is the consensus that the FA dehydrogenation mechanism over heterogeneous catalysts involves the deprotonation of FA to form metal-formate species, followed by C–H bond cleavage to release H_2 and CO_2.[13,14] Owing to the limitation of ionization equilibrium of FA, the dehydrogenation of FA can then occur only with the diluted FA, and be promoted by the base additives, such as NEt_3 and formate.[9-12] While since there is already plentiful Schiff base on our Au@Schiff-SiO_2 catalyst, which facilitates the O–H bond dissociation of FA to produce $CH_2=NH^{+}$– and metal-formate species, as a result, the extra addition of other additives, such as NEt_3 or potassium formate (PF), will not work anymore (Fig. S10, ESI†). On the other hand, different from other catalysts,[27] such Au@Schiff-SiO_2 catalyst was not effective for H_2 production from PF aqueous even at 80 ^{o}C (Fig. S11, ESI†). While when protonic acid, or even weak boric acid was added (Note that the addition of boric acid cannot produce FA in PF solutions), the production of H_2 can be triggered with the consumption of protonic H^{+}. It indicates that the protonated Schiff base $CH_2=NH^{+}$ might be involved in the C–H bond cleavage from formate species adsorbed on gold NPs, which is quite different from amine functionalized nanocatalyts. In addition, the electron modification of Schiff base toward gold NPs will lead to the increase of electron density of gold active centers to facilitate the formation of metal-formate, which enhances the rate of the catalytic dehydrogenation of FA.[5,28] As a result, a possible mechanism of FA dehydrogenation over our Schiff base functionalized gold nanocatalyst was proposed and schematically depicted in scheme 2. Due to the considerable quantity of Schiff base on the catalyst surface, electronegative nitrogen atoms could facilitate the O–H bond dissociation, leading to the formation of $CH_2=NH^{+}$– species. Such protonated Schiff base promotes the β-hydride elimination in the gold-formate complex to produce CO_2 and H_2, which is the rate-determining step in whole reaction and is achieved by the cooperation of Au and Schiff base at the interface of catalyst.



Scheme 2. A possible reaction mechanism was proposed for the dehydrogenation of FA by Au@Schiff-SiO_2.

Finally, we have also tested the durability of Au@Schiff-SiO_2 catalyst in the 10 M FA solutions at 50 ^{o}C (Fig. S12, ESI†). This Au@Schiff-SiO_2 catalyst keeps its excellent initial activity and H_2 production after more than five runs, suggesting the well recycling use of our catalyst. This may be attributed to its encapsulating structure of Au NPs on the Schiff base modified SiO_2 support, which prevents the aggregation and leaching of gold NPs during the dehydrogenation reaction (Fig. S13, ESI†). Meanwhile, the Schiff base on the catalyst surface was sufficiently stable during the reaction as indicated by the unchanged FT-IR spectra of Au@Schiff-SiO_2 after reaction (Fig. S1b, ESI†).

Conclusions

In summary, a Schiff base functionalized gold nanocatalyst was facilely synthesized and shown to have excellent activity for high-concentration FA dehydrogenation without any additives, which serves as a green and efficient catalyst for H_2 production in fuel cell application. The Schiff base for efficiently deprotonating of FA to metal-formate intermediates, and for promoting the cleavage of C-H with electronegative gold NPs was suggested to its unusual catalytic performance in FA dehydrogenation. What's more, the formed gold NPs with a encapsulating structure significantly increases the interfacial area between the Schiff base and gold NPs. These results can pave the way for rational design of new type of catalysts, as demonstrated here the Schiff base functionalized gold catalyst, for H_2 production via FA dehydrogenation.

Acknowledgements

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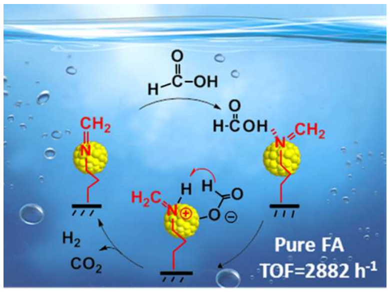
References

1 H. L. Jiang, S. K. Singh, J. M. Yan, X. B. Zhang, Q. Xu, ChemSusChem, 2010, 3, 541-549.
2 F. Jin, Y. Gao, Y. Jin, Y. Zhang, J. Cao, Z. Wei, Z. R.L. Smith Jr, Energy Environ. Sci., 2011, 4, 881-884.
3 M. Grasemann, G. Laurenczy, Energy Environ. Sci., 2012, 5, 8171-8181.
4 A. Bulut, M. Yurderi, Y. Karatas, M. Zahmakiran, H. Kivrak, M. Gulcan, M. Kaya, Appl. Catal. B: Environ., 2015, 164, 324-333.
5 M. Yurderi, A. Bulut, N. Caner, M. Celebi, M. Kaya, M. Zahmakiran, Chem. Commun., 2015, 51, 11417-11420.
6 B. Loges, A. Boddien, H. Junge, M. Beller, Angew. Chem. Int. Ed., 2008, 120, 4026–4029.
7 S. Enthaler, J. von Langermann, T. Schmidt, *Energy Environ. Sci.*, 2010, *3*, 1207-1217.
8 K. V. Kordesch, G. R. Simader, Chem. Rev., 1995, 95, 191-207.
9 Q. Y. Bi, X. L. Du, Y. M. Liu, Y. Cao, H. Y. He, K. N. Fan, J. Am. Chem. Soc., 2012, 134, 8926-8933.
10 Q. L. Zhu, N. Tsumori, Q. Xu, Chem. Sci., 2014, 5, 195-199.
11 K. Jiang, K. Xu, S. H. Zou, W. B. Cai, J. Am. Chem. Soc., 2014, 136, 4861-4864.
12 Y. Chen, Q. L. Zhu, N. Tsumori, Q. Xu, J. Am. Chem. Soc., 2015, 137, 106-109.
13 M. Martis, K. Mori, K. Fujiwara, W.S. Ahn, H. Yamashita, J. Phys. Chem. C, 2013, 117, 22805-22810.
14 K. Koh, J. E. Seo, J. H. Lee, A. Goswami, C. W. Yoon, T. Asefa, J. Mater. Chem. A, 2014, 2, 20444-20449.
15 S. Kumar, D.N. Dhar, P.N. Saxena, J. Sci. Ind. Res., 2009, 68, 181–187.
16 C. González‐Arellano, A. Corma, M. Iglesias, F. Sanchez, Eur. J. Inorg. Chem., 2008, 7, 1107-1115.
17 C. González‐Arellano, A. Corma, A. M. Iglesias, F. Sanchez, Adv. Synth. & Catal., 2004, 346, 1758-1764.
18 Y. Himeda, Green Chem., 2009, 11, 2018-2022.
19 T. Ishida, M. Haruta, Angew. Chem. Int. Ed., 2007, 46, 7154-7156.
20 X. Gu, Z. H. Lu, H. L. Jiang, T. Akita, Q. Xu, J. Am. Chem. Soc., 2011, 133, 11822-11825.
21 Z. L. Wang, J. M. Yan, Y. Ping, H. L. Wang, W. T. Zheng, Q. Jiang, Angew. Chem. Int. Ed., 2013, 52, 4406-4409.
22 M. Yadav, T. Akita, N. Tsumori, Q. Xu, J. Mater. Chem., 2012, 22, 12582-12586.
23 M. Ojeda, E. Iglesia, Angew. Chem. Int. Ed., 2009, 121, 4894-4897.
24 A. H. El-Masry, H. H. Fahmy, S.H. Ali Abdelwahed, Molecules, 2000, 5, 1429-1438.
25 S. Zhang, Ö. Metin, D. Su, S. Sun, *Angew. Chem. Int. Ed., 52*, 2013, 3681-3684.
26 C. M. Yang, M. Kalwei, F. Schüth, K. Chao, J. Appl. Catal. A: General, 2003, 254, 289-296.
27 Q. Y. Bi, J. D. Lin, Y. M. Liu, X. L. Du, J. Q. Wang, H. Y. He, Y. Cao, Angew. Chem. Int. Ed., 2014, 5*3*, 13583-13587.
28 J. S. Yoo, F. Abild-Pedersen, J. K. Nørskov, F. Studt, ACS Catal., 2014, 4, 1226-1233.



A novel Schiff base modified gold nanocatalyst was desighed for H_2 production from pure formic acid (FA) without any additives.