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Highly efficient hydrogenation of carbon dioxide to methyl formate over supported gold catalysts

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Transformation of carbon dioxide (CO_2) into valuable chemicals is an interesting topic in green chemistry. Hydrogenation of CO_2 to methyl formate (MF) in the presence of methanol is an important reaction. In this work, Au nanocatalysts immobilized on different supports were prepared and characterized by X-ray diffraction (XRD), transmission electron microscope (TEM) and X-ray photoelectron spectrometer (XPS). The catalytic performances of the catalysts for the reaction were studied. It was demonstrated that the Au/ZrO_2, Au/CeO_2 and Au/TiO_2 were very active and selective for the reaction in the absence of any basic additives. The Au/ZrO_2 was more active than Au/CeO_2 and Au/TiO_2 if the sizes of Au particles on the supports were similar. Moreover, for the Au/ZrO_2 catalysts, Au particles with smaller size had higher activity. The possible mechanism of the catalytic reaction was proposed.

Introduction

Carbon dioxide (CO_2) is the major greenhouse gas. On the other hand, it is also a nontoxic, abundant and inexpensive carbon source. Transformation of CO_2 into value-added chemicals is of vital importance. Different routes have been developed for the conversion of CO_2 into valuable products,[1] such as urea, formic acid,[2] methanol,[3] carbonate[4] and dimethylformamide.[5] With the progress in hydrogen generation from biomass[6] and splitting of water by photocatalysis,[7] hydrogenation of CO_2 to produce various chemicals will receive more and more attention.

Methyl formate (MF) is an important chemical with wide applications.[8,9] Currently, MF is produced by carbonylation of methanol with CO or by methanol dehydrogenation.[10] Synthesis of MF from CO_2, H_2 and methanol, which is shown in Equation (1), has been studied by different researchers. For example, Jessop *et al.*[11] used $RuCl_2(PMe_3)_4$ as the catalyst to synthesize MF and the TON could be 3500 in 60 hrs. Baiker and co-workers[12] carried out the reaction promoted by $[RuCl_2(dppe)_2]$. Federsel *et al.*[13] studied the reaction using bio-inspired iron based homogeneous catalyst and a TON of 292 for MF was obtained. Heldebrant[14] reported capture of CO_2 and subsequent homogeneous hydrogenation of CO_2 to MF catalyzed by $RuCl_2(PPh_3)_3$/DBU system. For these homogenous catalysts, a base (*e.g.* triethylamine) was used in the reaction. Heterogeneous catalysts have also been utilized to promote the reaction. It was shown that silica hybrid gel supported $RuCl_2[PMe_2(CH_2)_2Si(OEt)_3]_3$ was very effective for the reaction using triethylamine as the base.[15] Tsang *et al.*[16,17] demonstrated that Pd/Cu/ZnO and Cu/ZnO catalyst systems could fix CO_2 into MF in the absence of bases, but the catalytic activity was low and by-product CO was produced. Xin and co-workers *et al.* reported photocatalytic reduction of CO_2 to MF using ZnS[18] and CuO/TiO_2[19] as the catalysts. A study of photocatalytic reduction was also conducted over Bi_2S_3 prepared by solvothermal method.[20]

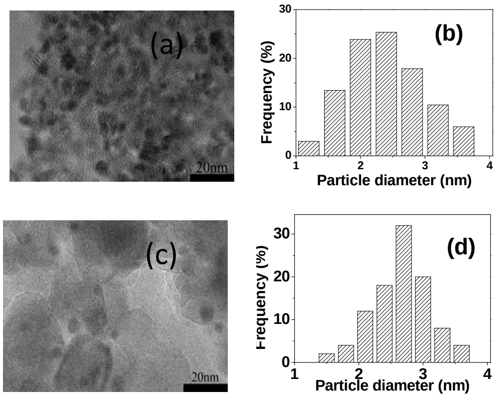
Gold based catalysts have attracted much attention due to their unique catalytic performance in oxidation of carbon monoxide,[21] hydrogenation of unsaturated compounds[22,23] and low temperature water gas shift reaction.[24] It was reported that Au/TiO_2 could catalyze hydrogenation of CO_2 to formic acid in the presence of an amine.[25] Formic acid can react with methanol to produce MF by esterification reaction. We expect that using Au as the catalyst, MF can be formed by hydrogenation of CO_2 in the presence of methanol without any basic additive. CeO_2, TiO_2, and ZrO_2 are commonly used supports for hydrogenation of carbon dioxide.[3c,5c] In this work, we studied the reaction of CO_2 with H_2 and methanol to produce MF. It was found that the supported gold catalysts Au/CeO_2, Au/TiO_2, and Au/ZrO_2 had very activity and selectivity for the reaction without use of any base. Especially, the Au/ZrO_2 with small Au particles was very active and selective for the reaction.

$$H_2+CO_2+CH_3OH\rightarrow HCOOCH_3+H_2O \qquad (1)$$

Results and discussion

In this work, we prepared Au/CeO_2 and Au/ZrO_2 using well established deposition-precipitation method.[26,27] The detailed procedures are described in Experimental section. In preparation of the Au/ZrO_2 catalysts, the pH values of the solutions were controlled at 9.0 and 10.5, respectively, and the corresponding catalysts are denoted as Au/ZrO_2-9.0 and Au/ZrO_2-10.5. The reduced Au/CeO_2, Au/ZrO_2-9.0, Au/ZrO_2-10.5, and commercial Au/TiO_2 catalyst were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM) and X-ray photoelectron spectrometer (XPS).

The TEM images of the catalysts are illustrated in Fig. 1. The sizes of the Au particles in the catalysts were evaluated by counting two hundred particles, and the size distributions are also presented in the figure. The average diameters of gold particles in the Au/CeO_2, Au/TiO_2, Au/ZrO_2-9.0 and Au/ZrO_2-10.5 were 2.5 nm, 2.6 nm, 1.9 nm, and 2.4 nm, respectively.



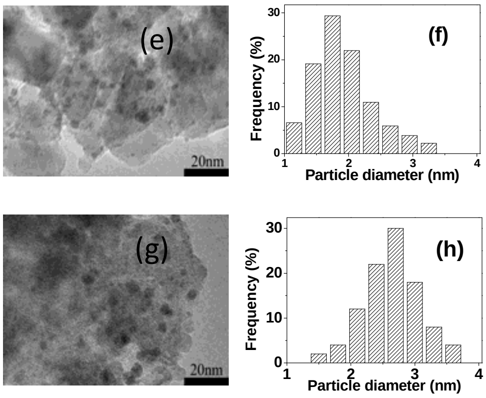


Fig. 1 The TEM images of catalysts and the size distributions of the Au particles. (a) and (b) Au/CeO_2; (c) and (d) Au/TiO_2; (e) and (f) Au/ZrO_2-9.0; (g) and (h) Au/ZrO_2-10.5.

Fig. 2 gives the XRD patterns of the catalysts. All the samples show characteristic peaks of corresponding supports (TiO_2, CeO_2 and ZrO_2). For all of the four catalysts, the peak of the gold particles was not observed, suggesting very small size. This is consistent with the conclusion obtained by the TEM observation.

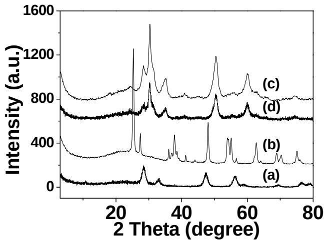


Fig. 2 The XRD patterns of the catalysts. (a) Au/CeO_2; (b) Au/TiO_2; (c) Au/ZrO_2-9; (d) Au/ZrO_2-10.5.

Fig. 3 shows the XPS spectra of the catalysts. As can be known from the figure, the Au $4f_{7/2}$ binding energies of the gold in Au/ZrO_2-9.0 and Au/ZrO_2-10.5 are 84.2 eV and 84.1 eV, respectively. The slightly difference may be attributed to the size effect.[28] The binding energies of gold $4f_{7/2}$ in the Au/TiO_2 and Au/CeO_2 are respectively 83.5 eV and 83.9 eV, which are lower than the value of bulk metal (84.0 eV), implying the electron transfer from supports to gold nanoparticles.

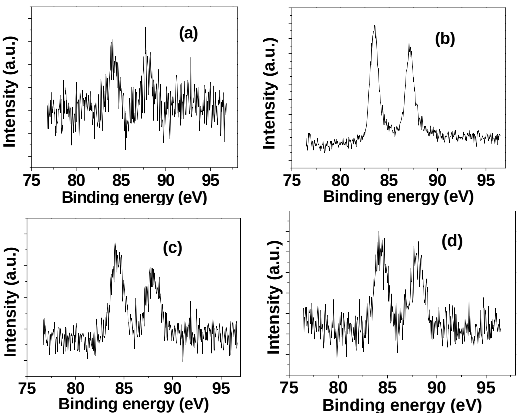


Fig. 3 XPS spectra of (a) Au/CeO_2, (b) Au/TiO_2, (c) Au/ZrO_2-9, and (d) Au/ZrO_2-10.5.

The turnover frequencies (TOFs, moles of MF formed per hour per mole of Au) of the reaction catalyzed by the Au nanocatalysts on different supports are compared in Fig. 4a. As discussed above, the Au particles in the Au/CeO_2, Au/TiO_2, Au/ZrO_2-10.5 have similar size. It can be concluded from the results in Fig. 4a that the activity of the Au particles on the ZrO_2 was considerably higher than that on the TiO_2 or CeO_2 when the size of the Au particles was similar. In general, CeO_2 is considered as basic and TiO_2 is nearly neutral[29-31] while ZrO_2 has amphoteric nature.[32] Therefore, the main reason for the higher activity of the Au particles on the ZrO_2 may be that the basic sites facilitate the adsorption and activation of CO_2 and the acidic sites promote desorption of formed formic acid, which will be discussed in the following.

Fig. 4a also shows that the activity of the Au/ZrO_2-9.0 is higher than that of the Au/ZrO_2-10.5. The main difference of the two catalysts is that the Au particles in the former have smaller size. This indicates that smaller size of the Au particles is favourable to accelerate the reaction. In this work, the effects of various factors on the reaction were further studied using Au/ZrO_2-9.0 as the catalyst.

Fig. 4b demonstrates dependence of the conversion of methanol on reaction time at 120 °C and 140 °C. The conversion increased with reaction time and a maximum conversion of 5.4% was reached at 120 °C. However, the maximum conversion was 4.0% at 140 °C. The standard Gibbs free energy of the overall reaction is 26.8 kJ/mol.[33] Therefore, the reaction is reversible and equilibrium conversion was reached. It can also be known from the figure that the equilibrium conversion at higher temperature is lower. This is easy to understand because the reaction is exothermic with standard reaction enthalpy of –10.5 kJ/mol.[33a] We also characterized the catalysts used after the reaction at 120 °C and 140 °C for 7 hrs by TEM, and the images are presented in the supporting information (Fig. S1), together with the TEM image of the catalyst before used (Fig. 1e) for comparison. The size of the Au particles did not change notably in the reaction, as can be known from Fig. 1 and S1.

Fig. 4c shows the effect of total pressure of CO_2 and H_2 on catalytic activity of the catalyst at 120 °C. It can be seen that the TOF increased with the total pressure. The main reason for this phenomenon is that the concentrations CO_2 and H_2 increased with pressure, which is favourable to the conversion of methanol.

The dependence of the TOF on reaction temperature is illustrated in Table 1. As expected, the TOF increased with increasing temperature. Our experiments showed that there was no by-product in the reaction at all of the temperatures. Cu/ZnO and Pd/Cu/ZnO were reported to be active for the reaction.[16,17] To the best of our knowledge, these were the only catalysts reported for the reaction without using basic additives. Comparing these catalysts, the gold based catalysts have obvious advantages. The activity of the catalysts is very high. For example, at 120 °C and 12 MPa, the TOF of the Au/ZrO_2-9.0 prepared in this work is 71 h^{-1}. At the similar condition, the TOFs of Pd/Cu/ZnO[16] and Cu/ZnO[17] were 3.47 h^{-1} (150 °C, total pressure 6 MPa) and 2.38 h^{-1} (150 °C, total pressure 13 MPa), respectively. In addition, the catalysts of this work had very high selectivity and no by-products were generated, while the catalysts Cu/ZnO and Pd/Cu/ZnO were reported to produce some by-products, such as CO.[16,17] This indicates that the supported Au nanocatalysts have unique feature for the reaction. The main reason may be that Au is much more efficient than Cu for the generation of formic acid, which can react easily with methanol to form MF at the reaction condition.

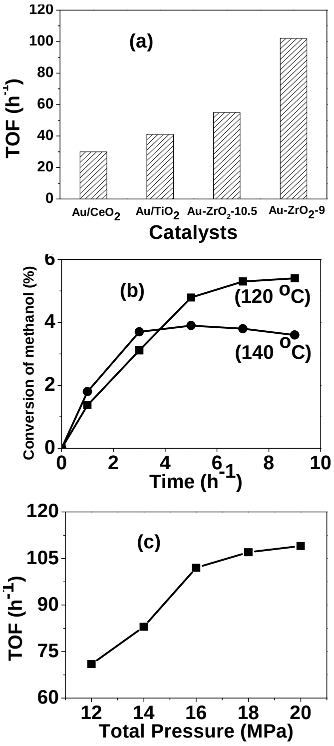


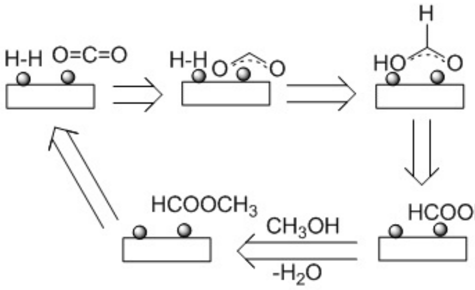
Fig. 4 The influence of reaction conditions on reaction. (a) The TOF values of the catalysts with different supports (P_{H2}=8 MPa, P_T=16 MPa, 120 ^oC, 80 mg catalysts, 3 hrs); (b) effect of reaction time on the conversion of methanol (P_{H2}=8 MPa, P_T=16 MPa, 80 mg Au/ZrO$_2$-9.0 at 120 ^oC, 60 mg Au/ZrO$_2$-9.0 at 140 ^oC); (c) effect of the reaction pressure on the TOF values (120 ^oC, 80 mg Au/ZrO$_2$-9.0, 3 hrs).

Table 1 Reaction results at different temperatures

Entry	P_{H2} (MPa)	P_T (MPa)^a	T (^oC)	Time (h)	Selectivity	TOF (h^{-1})^b
1	8	16	60	3	>99.9%	4
2	8	16	80	3	>99.9%	14
3	8	16	100	3	>99.9%	40
4	8	16	120	3	>99.9%	102
5^c	8	16	140	1	>99.9%	204
6^d	8	16	160	1	>99.9%	309
7^e	8	16	180	1	>99.9%	430
8^f	8	16	200	1	>99.9%	534

[a] Total pressure of hydrogen and CO_2 at reaction temperature, [b] TOF values denotes moles of MF per mole of gold per hour, [c-f] reactions conducted using 60 mg, 40 mg, 30 mg, and 20 mg Au-ZrO$_2$-9.0 as the catalyst, respectively.

It is interesting to study the reaction mechanism promoted by the Au catalysts. It has been reported that Au based catalysts have satisfactory catalytic activity for the hydrogenation reactions of unsaturated carbonyl compounds, alkynes and nitroaromatics.[34] Hydrogen can be dissociated on low coordinated Au surface sites[35] and H_2 are activated more efficiently when the Au particle was smaller than 2 nm.[36] Based on the results of this work and the related researches reported in the literature, we propose a possible mechanism for this reaction, as is shown in Scheme 1. The CO_2 was activated mainly by the interaction of its oxygen atoms with catalysts. Formic acid is first formed on Au particles.[25] Then, esterification reaction between the formic acid and methanol takes place. It is known that generation of formic acid from hydrogenation of CO_2 is a thermodynamically unfavourable reaction.[2a] However, the formed MF moves away from the surface of the catalyst. Therefore, the formic acid intermediate can be yielded continuously until the equilibrium of the reaction shown in Eq. (1) is reached. Thus, effective activation of hydrogen and CO_2 and desorption of the MF are all important for the reaction.



Scheme 1 Possible mechanism for the formation of MF from CO_2, hydrogen and methanol over Au catalyst.

Conclusion

The synthesis of MF from CO_2, H_2, and methanol catalyzed by supported Au nanocatalysts has been carried for the first time. All the catalysts, Au/ZrO$_2$, Au/CeO$_2$ and Au/TiO$_2$ have very high activity and selectivity for the reaction in wide temperature and pressure ranges without any basic additives. The performances of the catalysts depend considerably on the characters of the supports and the size of the Au nanopartices. The TOF of the Au/ZrO$_2$ with an average Au size of 1.9 nm can be higher than 200 h^{-1} at 140 ^oC and 16 MPa. The catalytic reaction may include mainly formation of formic acid intermediate and esterification of formic acid and methanol.

Experimental details

Materials

$ZrOCl_2 \cdot 8H_2O$ (A. R. grade) and $HAuCl_4 \cdot 4H_2O$ (A. R. grade) were purchased from Sinopharm Chemical Reagent Co. Ltd. Ammonia aqueous solution (28%), urea, ammonia cerium nitrate, DMF, n-butanol, and methanol were all A. R. grade and provided by Beijing Chemical Reagent Company. The CO_2 (>99.99%), H_2 (>99.99%), and N_2 (>99.95%) were supplied by Beijing Analytical Instrument Company. All the chemicals were used as received without further purification.

Catalyst preparation

The ZrO_2 support was prepared by the methods reported in literature.[27] The Au/ZrO$_2$-9.0 was fabricated by deposition-precipitation method[27] with minor modification.

Briefly, 1.0 g ZrO_2 support was added to 60 mL $HAuCl_4$ aqueous solution of 0.8 mmol/L, and then the pH value was adjusted to 9.0 by addition of 0.25 mol/L ammonia solution drop by drop. After stirring at room temperature for 6 hours, the solid was filtrated and washed for 5 times using deionized water. The sample was dried at 40°C under N_2 flow for 12 hours. The Au/ZrO_2-9.0 was obtained after reduction in H_2 flow for 2 hours at 250 °C. The gold loading in the catalyst was 0.8 wt% as determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

The procedure to prepare the Au/ZrO_2-10.5 was similar to that used to fabricate Au/ZrO_2-9.0. The only difference was that the pH value of the solution was adjusted to 10.5, instead of 9.0. The content of the gold in the Au/ZrO_2 determined by ICP-AES was 0.8 wt%.

Ceria support and Au/CeO_2 catalyst was prepared by deposition-precipitation method[26,37] with some modification. Briefly, 1.0 g CeO_2 was immersed in 100 mL $HAuCl_4$ aqueous solution of 0.5 mmol/L, and the pH value of the solution was adjusted to 9.0 by adding 0.02 mol/L NaOH solution. After stirring at 70 °C for 2 hours, the solid was filtrated and washed for 5 times using deionized water. The sample was dried at 40 °C under N_2 flow for 12 hours. The Au/CeO_2 was obtained after reduction in H_2 flow for 2 hours at 250 °C. The content of in the Au/CeO_2 was 0.78 wt% as determined by ICP-AES.

The Au/TiO_2 catalyst with 1.0 wt% Au was supplied by AUROlite Corporation.

Sample characterization

The gold content in the catalysts was determined by ICP-AES (PROFILE SPEC, Leeman). The XRD characterization was carried out on Rigaku D/max 2500 with nickel filtered Cu-Kα (λ=0.154 nm) operated at 40 kV and 20 mA. The XPS analysis was performed using ESCALab 220I-XL equipment electron spectrometer from VG Scientific using 300 W AlKα radiation with a hemispherical energy analyzer. The binding energies were calibrated with the C1s line at 284.8 eV from contaminated carbon element. The TEM images of the catalysts were measured on JEOL-2100F electron microscopy operated at 200 kV.

Reaction

The reaction was carried out in a Teflon-lined stainless steel reactor of 16 mL, which was similar to that used previously.[38] In a typical experiment, 1.0 g methanol, desired amount of catalyst was added into the reactor. The air in the reactor was replaced by H_2. Then the reactor was placed in an air bath of desired temperature. After stabilization for 1 hour, the H_2 and CO_2 gas were charged into the reactor and the stirrer was started with a speed of 500 rpm. After the certain reaction time, the reactor was placed in ice-water mixture and the gas was released slowly through DMF cold trap to capture the MF in the gas flow. The gas sample was collected in a gas bag. The liquid in the cold trap was mixed with that in the reactor, and the mixture was analyzed quantitatively by GC (Agilent 6820) equipped with a flame ionization detector (FID) and a PEG-20M capillary column. n-Butanol was used as external standard. The gas sample was analyzed on GC with TCD detector.

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Note and references:

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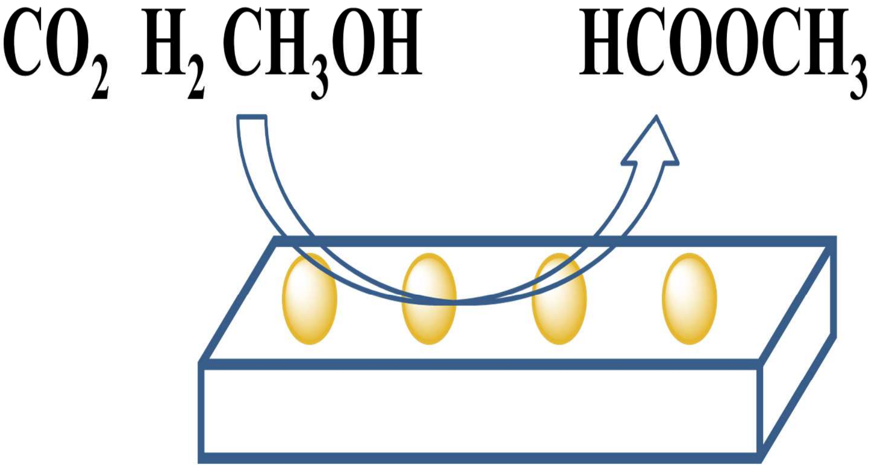
1. (a) W. Wang, S. P. Wang, X. B. Ma and J. L. Gong, *Chem. Soc. Rev*., 2011, **40**, 3703-3727; (b) T. Sakakura, J. C. Choi and H. Yasuda, *Chem. Rev*., 2007, **107**, 2365-2387; (c) C. Federsel, R. Jackstell and M. Beller, *Angew. Chem. Int. Ed*., 2010, **49**, 6254-6257; (d) M. Y. He, Y. H. Sun, and B. X. Han, *Angew. Chem. Int. Ed*., 2013, **52**, 9620-9633. (e) M.Aresta, A. Dibenedetto and A. Angelini, *Chem. Rev*., 2014, **114**, 1709-1742.
2. (a) Z. F. Zhang, Y. Xie, W. J. Li, S. Q. Hu, J. L. Song, T. Jiang and B. X. Han, *Angew. Chem. Int. Ed*., 2008, **47**, 1127-1129; (b) T. Schaub and R. A. Paciello, *Angew. Chem. Int. Ed*., 2011, **50**, 7278-7282; (c) P. G. Jessop, T. Ikariya and R. Noyori, *Nature*, 1994, **368**, 231-233; (d) P. G. Jessop, Y. Hsiao, T. Ikariya and R. Noyori, *J. Am. Chem. Soc*., 1996**, 118**, 344-355; (e) R. Tanaka, M. Yamashita and K. Nozaki, *J. Am. Chem. Soc*., 2009, **131**, 14168-14169; (f) C. Ziebart, C. Federsel, P. Anbarasan, R. Jackstell, W. Baumann, A. Spannenberg and M. Beller, *J. Am. Chem. Soc*., 2012, **134**, 20701-20704; (g) M. S. Jeletic, M. T. Mock, A. M. Appel and J. C. Linehan, *J. Am. Chem. Soc*., 2013, **135**, 11533-11536; (h) S. Wesselbaum, U. Hintermair and W. Leitner, *Angew. Chem. Int. Ed*., 2012, **51**, 8585-8588.
3. (a) F. Studt, I. Sharafutdinov, F. Abild-Pedersen, C. F. Elkjær, J. S. Hummelshøj, S. Dahl, I. Chorkendorff, J. K. Nørskov, *Nature Chem*., 2014, **6**, 320-324; (b) S. Wesselbaum, T. vom Stein, J. Klankermayer, W. Leitner, *Angew. Chem. Int. Ed*., 2012, **51**, 7499-7502; (c) J. Graciani, K. Mudiyanselage, F. Xu, A. E. Baber, J. Evans, S. D. Senanayake, D.J. Stacchiola, P. Liu, J. Hrbek, J. F. Sanz and J. A. Rodriguez, *Science*, 2014, **345**, 546-550.
4. (a) Y. Xie, Z. F. Zhang, T. Jiang, J. L. He, B. X. Han, T. B. Wu, K. L. Ding, *Angew. Chem. Int. Ed*., 2007, **46**, 7255-7258; (b) Q. W. Song, L. N. He, J. Q. Wang, H. Yasuda, T. Sakakura, *Green Chem*., 2013, **15,** 110-115; (c) K. R. Roshan, G. Mathai, J. Kim, J. Tharun, G. A. Park and D. W. Park, *Green Chem*., 2012, **14**, 2933-2940; (d) M. R. Reithofer, Y. N. Sum and Y. G. Zhang, *Green Chem*., 2013, **15**, 2086-2090.
5. (a) P. G. Jessop, F. Joo and C. Tai, Coord. *Chem. Rev*., 2004, **248**, 2425-2442; (b) J. L. Liu, C. K. Guo, Z. F. Zhang, T. Jiang, H. Z. Liu, J. L. Song, H. L. Fan and B. X. Han, *Chem. Commun*., 2010, **46**, 5770-5772; (c) Q. Y. Bi, J. D. Lin, Y. M. Liu, S. H. Xie, H. Y. He and Y. Cao, *Chem. Commun*., 2014, **50**, 9138-9140.

6. J. S. M.Campo, J. Rollin, S. Myung, Y. Chun, S. Chandrayan, R. Patino, M. W. W. Adams and Y. H. P. Zhang, *Angew. Chem. Int. Ed*., 2013, **52**, 1-5.
7. A. Primo, T. Marino, A. Corma, R. Molinari and H. García, *J. Am. Chem. Soc*., 2011, **133**, 6930-6933.
8. C. H. Han, X. Z. Yang, G. J. Gao, J. Wang, H. L. Lu, J. Liu, M. Tong and X. Y. Liang, *Green Chem.*, 2014, **16**, 3603-3615.
9. A. Wittstock, V. Zielasek, J. Biener, C. M. Friend and M. Bäumer, *Science*, 2010, **327**, 319-322.
10. P. G. Jessop, T. Ikariya and R. Noyori, *Chem. Rev*., 1995, **95**, 259-272.
11. P. G. Jessop, Y. Hsiao, T. Ikariya and R. Noyori, *J. Chem. Soc., Chem. Commun*., 1995, 707-708.
12. O. Krocher, R. A. Koppel and A. Baiker, *Chem.Commun*., 1997, 453-454.
13. C. Federsel, A. Boddien, R. Jackstell, R. Jennerjahn, P. J. Dyson, R. Scopelliti, G. Laurenczy and M. Beller, *Angew. Chem. Int. Ed*., 2010, **49**, 9777-9780.
14. M. Yadav, J. C. Linehan, A. J. Karkamkar, E. V. Eide and D. J. Heldebrant, *Inorg. Chem*., 2014, **53**, 9849-9854.
15. O. Krocher, R. A. Koppel, M. Froba and A. Baiker, *J. Catal*., 1998, **178**, 284-298.
16. K. M. K. Yu, C. M. Y. Yeung and S. C. Tsang, *J. Am. Chem. Soc*., 2007, **129**, 6360-6361.
17. K. M. K. Yu and S. C. Tsang, *Catal. Lett*., 2011, **141**, 259-265.
18. J. S. Chen, F. Xin, S. Y. Qin and X. H. Yin, *Chem. Eng. J*., 2013, **230**, 506-512.
19. S. Y. Qin, F. Xin, Y. D. Liu, X. H. Yin and W. Ma, *J. Colloid. Interface. Sci*., 2011, **356**, 257-261.
20. J. S. Chen, S. Y. Qin, G. X. Song, T. Y. Xiang, F. Xin and X. H. Yin, *Dalton Trans*., 2013, **42**, 15133-15138.
21. M. Valden, X. Lai and D. W. Goodman, *Science*, 1998, **281**, 1647-1650.
22. M. Boronat, P. Concepcion, A. Corma, S. Gonzalez, F. Illas and P. Serna, *J. Am. Chem. Soc*., 2007, **129**, 16230-16237.
23. A. Corma, P. Serna and H. Garcia, *J. Am. Chem. Soc*., 2007, **129**, 6358-6359.
24. H. Sakurai, A. Ueda, T. Kobayashi and M. Haruta, *Chem. Commun*., 1997, **33**, 271-272.
25. D. Preti, C. Resta, S. Squarcialupi and G. Fachinetti, *Angew. Chem. Int. Ed*., 2011, **50**, 12551-12554.
26. N. Ta, J. Y. Liu, S. Chenna, P. A. Crozier, Y. Li, A. L. Chen and W. J. Shen, *J. Am. Chem. Soc*., 2012, **134**, 20585-20588.
27. Q. Y. Bi, X. L. Du, Y. M. Liu, Y. Cao, H. Y. He and K. N. Fan, *J. Am. Chem. Soc*., 2012, **134**, 8926-8933.
28. G. K. Wertheim and S. B. DiCenzo, *Phys. Rev. B*., 1988, **37**, 844-847.
29. K. C. Petallidou, K. Polychronopoulou, S. Boghosian, S. G. Rodriguez and A. M. Efstathiou, *J. Phys. Chem. C*, 2013, **117**, 25467-25477.
30. K. P. Yu, W. Y. Yu, M. C. Kuo, Y. C. Liou and S. H. Chien, *Appl. Catal., B*, 2008, **84**, 112-118.
31. X. J. Liu, R. Wang, L. Y. Song, H. He, G. Z. Zhang, X. H. Zi and W. G. Qiu, *Catal. Commun*., 2014, **46**, 213-218.
32. (a) G. Postole, B. Chowdhury, B. Karmakar, K. Pinki, J. Banerji and A. Auroux, *J. Catal*., 2010, **269**, 110-121; (b) E. I. R. Medgaarden, W. V. Knowles, T. Kim, M. S. Wong, W. Zhou, C. J. Kiely and I. E. Wachs, *J. Catal*., 2008, **256**, 108-125.
33. (a) D. R. Lide, *CRC Handbook of Chemistry & Physics (84th)*, CRC press, 2003-2004; (b) C. L. Yaws, *Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Compounds*, Knovel, 2005.
34. T. Mitsudome and K. Kaneda, *Green Chem*., 2013, **15**, 2636-2654.
35. A. Corma, M. Boronat, S. Gonzalezb and F. Illas, *Chem. Commun*., 2007, **43**, 3371-3373.
36. T. Fujitani, I. Nakamura, T. Akita, M. Okumura and M. Haruta, *Angew. Chem. Int. Ed*., 2009, **48**, 9515-9518.
37. N. Ta, M. L. Zhang, J. Li, H. J. Li, Y. Li and W. J. Shen, *Catal. Today*, 2009, **148**, 179-183.
38. J. Ma, B. X. Han, J. L. Song, J. Y. Hu, W. J. Lu, D. Z. Yang, Z. F. Zhang, T. Jiang, M. Q. Hou, *Green Chem.***,** 2013, **15**, 1485-1489.

TOC



Supported gold catalysts show excellent efficiency in methyl formate synthesis from carbon dioxide, hydrogen and methanol.