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Discovery of a Ni-Ga catalyst for carbon dioxide reduction to methanol

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Abstract

The use of methanol as a fuel and chemical feedstock could become very important in the development of a more sustainable society if methanol could be efficiently obtained from the direct reduction of CO_2 using solar-generated hydrogen. If hydrogen production is to be decentralized, small-scale CO_2 reduction devices are required that operate at low pressures. Here, we report the discovery of a Ni-Ga catalyst that reduces CO_2 to methanol at ambient pressure. The catalyst was identified through a descriptor-based analysis of the process and the use of computational methods to identify Ni-Ga intermetallic compounds as stable candidates with good activity. We synthesized and tested a series of catalysts and found that Ni_5Ga_3 is particularly active and selective. Comparison with conventional Cu/ZnO/Al_2O_3 catalysts revealed the same or better methanol synthesis activity, as well as considerably lower production of CO. We suggest that this is a first step towards the development of small-scale low-pressure devices for CO_2 reduction to methanol.

References

1. Schlögl, R. Chemistry's role in regenerative energy. *Angew. Chem. Int. Ed.* **50**, 6424–6426 (2011).
2. Olah, G. A. Towards oil independence through renewable methanol chemistry. *Angew. Chem. Int. Ed.* **52**, 104–107 (2013).
3. Benson, E. E., Kubiak, C. P., Sathrum, A. J. & Smieja, J. M. Electrocatalytic and homogeneous approaches to conversion of CO_2 to liquid fuels. *Chem. Soc. Rev.* **38**, 89–99 (2009).
4. Arakawa, H. *et al*. Catalysis research of relevance to carbon management: progress, challenges, and opportunities. *Chem. Rev.* **101**, 953–996 (2001).
5. Hori, Y., Kikuchi, K. & Suzuki, S. Production of CO and CH_4 in electrochemical reduction of CO_2 at metal electrodes in aqueous hydrocarbonate solution. *Chem. Lett.* **14**, 1695–1698 (1985).
6. Kuhl, K. P., Cave, E. R., Abram, D. N. & Jaramillo, T. F. New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces. *Energy Environ. Sci.* **5**, 7050–7059 (2012).
7. Rosen, B. A. *et al*. Ionic liquid-mediated selective conversion of CO_2 to CO at low overpotentials. *Science* **334**, 643–644 (2011).
8. Cole, E. B. *et al*. Using a one-electron shuttle for the multielectron reduction of CO_2 to methanol: kinetic, mechanistic, and structural insights. *J. Am. Chem. Soc.* **132**, 11539–11551 (2010).
9. Schouten, K. J. P., Kwon, Y., van der Ham, C. J. M., Qin, Z. & Koper, M. T. M. A new mechanism for the selectivity to C(1) and C(2) species in the electrochemical reduction of carbon dioxide on copper electrodes. *Chem. Sci.* **2**, 1902–1909 (2011).
10. Chen, Y., Li, C. W. & Kanan, M. W. Aqueous CO_2 reduction at very low overpotential on oxide-derived Au nanoparticles. *J. Am. Chem. Soc.* **134**, 19969–19972 (2012).
11. Peterson, A. A. & Nørskov, J. K. Activity descriptors for CO_2 electroreduction to methane on transition-metal catalysts. *J. Phys. Chem. Lett.* **3**, 251–258 (2012).
12. Lewis, N. S. & Nocera, D. G. Powering the planet: chemical challenges in solar energy utilization. *Proc. Natl Acad. Sci. USA* **103**, 15729–15735 (2006).
13. Crabtree, G. & Sarrao, J. The road to sustainability. *Physics World* **22**, 24–30 (2009).
14. Hansen, J. B. & Nielsen, P. E. H. in *Handbook of Heterogeneous Catalysis* (eds Ertl, G., Knözinger, H. & Schüth, F.) 2920 (Wiley, 2008).
15. Kasatkin, I., Kurr, P., Kniep, B., Trunschke, A. & Schlögl, R. Role of lattice strain and defects in copper particles on the activity of $Cu/ZnO/Al_2O_3$

catalysts for methanol synthesis. *Angew. Chem. Int. Ed.* **46**, 7324–7327 (2007).

16. Behrens, M. Meso- and nano-structuring of industrial Cu/ZnO/(Al_2O_3) catalysts. *J. Catal.* **267**, 24–29 (2009).
17. Kurtz, M., Wilmer, H., Genger, T., Hinrichsen, O. & Muhler, M. Deactivation of supported copper catalysts for methanol synthesis. *Catal. Lett.* **86**, 77–80 (2003).
18. Campbell, C. T., Daube, K. A. & White, J. M. Cu/ZnO(0001) and ZnO_x/Cu(111): model catalysts for methanol synthesis. *Surf. Sci.* **182**, 458–476 (1987).
19. Bowker, M., Hadden, R. A., Houghton, H., Hyland, J. N. K. & Waugh, K. C. The mechanism of methanol synthesis on copper/zinc oxide/alumina catalysts. *J. Catal.* **109**, 263–273 (1988).
20. Askgaard, T. S., Nørskov, J. K., Ovesen, C. V. & Stoltze, P. A kintic model of methanol synthesis. *J. Catal.* **156**, 229–242 (1995).
21. Fisher, I. A. & Bell, A. T. *In-situ* infrared study of methanol synthesis from H_2/CO_2 over Cu/SiO_2 and $Cu/ZrO_2/SiO_2$. *J. Catal.* **172**, 222–237 (1997).
22. Meitzner, G. & Iglesia, E. New insights into methanol synthesis catalysts from X-ray absorption spectroscopy. *Catal. Today* **53**, 433–441 (1999).
23. Fujitani, T. & Nakamura, J. The chemical modification seen in the Cu/ZnO methanol synthesis catalysts. *Appl. Catal. A* **191**, 111–129 (2000).
24. Grunwaldt, J-D., Molenbroek, A. M., Topsøe, N-Y., Topsøe, H. & Clausen, B. S. *In situ* investigations of structural changes in Cu/ZnO catalysts. *J. Catal.* **194**, 452–460 (2000).
25. Hansen, P. L. *et al*. Atom-resolved imaging of dynamic shape changes in supported copper nanocrystals. *Science* **295**, 2053–2055 (2002).
26. Kurtz, M. *et al*. New synthetic routes to more active Cu/ZnO catalysts used for methanol synthesis. *Catal. Lett.* **92**, 49–52 (2004).
27. Waugh, K. C. Methanol synthesis. *Catal. Lett.* **142**, 1153–1166 (2012).
28. Yang, Y., Mims, C. A., Mei, D. H., Peden, C. H. F. & Campbell, C. T. Mechanistic studies of methanol synthesis over Cu from $CO/CO_2/H_2/H_2O$ mixtures: the source of C in methanol and the role of water. *J. Catal.* **298**, 10–17 (2013).
29. Grabow, L. C. & Mavrikakis, M. Mechanism of methanol synthesis on Cu through CO_2 and CO hydrogenation. *ACS Catal.* **1**, 365–384 (2011).
30. Behrens, M. *et al*. The active site of methanol synthesis over Cu/ZnO/Al_2O_3 industrial catalysts. *Science* **336**, 893–897 (2012).
31. Grabow, L. C. *et al*. Descriptor-based analysis applied to HCN synthesis from NH_3 and CH_4. *Angew. Chem. Int. Ed.* **50**, 4601–4605 (2011).
32. Lausche, A. C., Hummelshøj, J. S., Abild-Pedersen, F., Studt, F. & Nørskov, J. K. Application of a new informatics tool in heterogeneous catalysis: analysis of methanol dehydrogenation on transition metal catalysts for the production of anhydrous formaldehyde. *J. Catal.* **291**, 133–137 (2012).
33. Hammer, B., Hansen, L. B. & Nørskov, J. K. Improved adsorption energetics within density-functional theory using revised Perdew–Burke–Ernzerhof functionals. *Phys. Rev. B* **59**, 7413–7421 (1999).
34. Nørskov, J. K. *et al*. The nature of the active site in heterogeneous metal catalysis. *Chem. Soc. Rev.* **37**, 2163–2171 (2008).

35. Studt, F., Abild-Pedersen, F., Varley, J. B. & Nørskov, J. K. CO and CO_2 hydrogenation to methanol calculated using the BEEF–vdW functional. *Catal. Lett.* **143**, 71–73 (2013).

36. Wellendorff, J. *et al*. Density functionals for surface science: exchange-correlation model development with Bayesian error estimation. *Phys. Rev. B* **85**, 235149 (2012).

37. Nørskov, J. K., Abild-Pedersen, F., Studt, F. & Bligaard, T. Density functional theory in surface chemistry and catalysis. *Proc. Natl Acad. Sci. USA* **108**, 937–943 (2011).

38. Studt, F. *et al*. Identification of non-precious metal alloy catalysts for selective hydrogenation of acetylene. *Science* **320**, 1320–1322 (2008).

39. Okamoto, H. Ga-Ni (gallium-nickel). *J. Phase Equilib. Diffus.* **31**, 575–576 (2010).

40. Baltes, C., Vukojević, S. & Schüth, F. Correlations between synthesis, precursor, and catalyst structure and activity of a large set of CuO/ZnO /Al_2O_3 catalysts for methanol synthesis. *J. Catal.* **258**, 334–344 (2008).

41. Arico, A. S., Srinivasan, S. & Antonucci, V. DMFCs: from fundamental aspects to technology development. *Fuel Cells* **1**, 133–161 (2001).

42. Kamarudin, S. K., Daud, W. R. W., Ho, S. L. & Hasran, U. A. Overview on the challenges and developments of micro-direct methanol fuel cells (DMFC). *J. Power Sources* **163**, 743–754 (2007).

43. Lackner, K. S. A guide to CO_2 sequestration. *Science* **300**, 1677–1678 (2003).

44. Keith, D. W. Why capture CO_2 from the atmosphere? *Science* **325**, 1654–1655 (2009).

45. Jones, C. W. CO_2 capture from dilute gases as a component of modern global carbon management. *Annu. Rev. Chem. Biomol. Eng.* **2**, 31–52 (2011).

46. House, K. Z. *et al*. Economic and energetic analysis of capturing CO_2 from ambient air. *Proc. Natl Acad. Sci. USA* **108**, 20428–20433 (2011).

47. Studt, F. *et al*. CO hydrogenation to methanol on Cu-Ni catalysts: theory and experiment. *J. Catal.* **293**, 51–60 (2012).

48. Hummelshøj, J. S., Abild-Pedersen, F., Studt, F., Bligaard, T. & Nørskov, J. K. CatApp: a web application for surface chemistry and heterogeneous catalysis. *Angew. Chem. Int. Ed.* **51**, 272–274 (2012).

49. Peterson, A. A., Abild-Pedersen, F., Studt, F., Rossmeisl, J. & Nørskov, J. K. How copper catalyzes the electroreduction of carbon dioxide into hydrocarbon fuels. *Energy Environ. Sci.* **3**, 1311–1315 (2010).

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Contributions

F.S., F.A-P., J.S.H. and J.K.N. contributed to the computational work in this article. I.S., C.F.E., S.D. and I.C. contributed to the experimental work.

Competing financial interests

The authors declare no competing financial interests.

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Supplementary information

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1. Supplementary information (2,689 KB)
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