JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Subscriber access provided by Queen's University Library

Communication

Highly Efficient and Robust Au/MgCuCr2O4 Catalyst for Gas-Phase Oxidation of Ethanol to Acetaldehyde

Peng Liu, and Emiel J. M. Hensen

J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/ja406820f • Publication Date (Web): 06 Sep 2013

Downloaded from http://pubs.acs.org on September 10, 2013

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

ACS Publications
High quality. High impact.

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Highly Efficient and Robust Au/$MgCuCr_2O_4$ Catalyst for Gas-Phase Oxidation of Ethanol to Acetaldehyde

Peng Liu,*,† and Emiel J. M. Hensen*,†

†Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Supporting Information Placeholder

ABSTRACT: Gold nanoparticles (AuNP) supported on spinel $MgCuCr_2O_4$ are highly active and selective for the oxidation of ethanol with molecular oxygen to acetaldehyde (conversion 100%; yield ~95%). The catalyst is shown to be stable for at least 500 h. The unprecedented catalytic performance is understood in terms of strong synergy between metallic AuNPs and surface Cu^+ species. X-ray photoelectron spectroscopy shows that Cu^+ is already formed during catalyst preparation and becomes more dominant at the surface during the ethanol oxidation reaction. These Cu^+ species are stabilized at the surface of the ternary $MgCuCr_2O_4$-spinel support. Further kinetic measurements indicate that the Cu^+ species act as sites for O_2 activation.

Production of chemicals and fuels from abundant, renewable biomass and its derivatives provides a viable route to alleviate our strong dependence on depleting fossil fuels.[1] For this purpose, ethanol is particularly attractive because of its facile synthesis by biomass fermentation and expected increased availability and reduced cost.[2] Selective oxidation of ethanol to acetaldehyde (CH_3CHO), acetic acid and ethyl acetate is of great interest for the chemical industry to decrease the use of petrochemical reserves.[3] In particular, acetaldehyde is an important bulk chemical for the production of peracetic acid, pentaerythritol, pyridine bases, butylene glycol and chloral, with a worldwide production over 10^6 tons/year.[4] Currently, production of acetaldehyde is mainly by the Wacker process, via oxidation of ethylene in strong acidic solutions catalyzed by palladium and copper chlorides.[5] Here, a promising opportunity arises to replace petroleum-based ethylene by renewable ethanol for more green and sustainable acetaldehyde production.

Recently, the use of supported gold nanoparticles (AuNP) to catalyze aerobic oxidation of alcohols has become the center of attention.[6] AuNP catalysts have, in particular, shown promise for selective oxidation of ethanol with molecular oxygen.[7-15] Liquid-phase ethanol oxidation mainly yields acetic acid or ethyl acetate, but supported AuNP catalysts suffer deactivation upon reuse due to gold sintering under hydrothermal conditions.[7] A more attractive process for industrial application would be gas-phase ethanol oxidation because of the convenience of catalyst separation, solvent-free conditions and facile continuous process operation.[16] The most significant disadvantage of current gold-based catalysts would appear to be the high reaction temperature, which tends to cause low selectivity and deactivation. For instance, Stucky reported that 6.3 nm Au/SiO_2 showed an ethanol conversion of 45% with 75% acetaldehyde selectivity at 200 ^oC.[10] Au/TiO_2 (~2 nm) was able to convert 60% of an ethanol feed at ~120 ^oC; full conversion was reached at 280 ^oC, but under these conditions the catalyst gradually deactivated and selectivity was below 80%.[12] Among various unitary oxide supported AuNP catalysts, Au/MoO_3 showed the highest acetaldehyde yield (>90% at 240 ^oC), but without evidence of catalyst stability.[14] More recently, pre-oxidized bimetallic Au-Cu/SiO_2 catalysts were reported to be active and stable for ethanol conversion (~90%) with ~85% acetaldehyde selectivity at 200 ^oC for 50 h on-stream.[15] However, these catalyst systems are far from practical application, mainly because of the low ethanol concentration (< 1 vol%)[14], the low acetaldehyde selectivity (< 90%)[10-13,15] and/or the low gas hourly space velocity (GHSV < 10,000 mL g_{cat}^{-1} h^{-1})[10,12,13,15].

In this report, we present a ternary spinel ($MgCuCr_2O_4$) supported AuNP catalyst that is capable of achieving ~100% ethanol conversion with ~95% acetaldehyde selectivity at 250 ^oC of a feed of 1.5 vol% ethanol at a GHSV of ~ 100,000 mL g_{cat}^{-1} h^{-1}. The catalyst is very stable for at least 500 h (Figure 1). The unprecedented catalytic performance relates to synergy between AuNP and surface Cu^+ species, which facilitates O_2 activation. The $MgCuCr_2O_4$ spinel stabilizes Cu^+ formed during catalyst preparation and ethanol oxidation and also ensures high and stable AuNP dispersion.

Chromite-spinels were chosen primarily because of the potential shown in our previous work on hydrotalcite supported AuNP catalysts for liquid-phase aerobic oxidation of alcohols.[17] The strong synergy between MgCr-hydrotalcite and AuNP motivated us to explore the gas-phase ethanol oxidation on MgCr-based oxides (typically $MgCr_2O_4$ spinel) supported gold catalysts. To date, no chromite-spinel supported AuNP catalysts were reported for ethanol oxidation.[18] We prepared several $Mg_{0.75}M_{0.25}Cr_2O_4$ spinels (denoted as $MgMCr_2O_4$, M = Co, Ni, Cu) with the same structure as $MgCr_2O_4$ by a coprecipitation-calcination method, which was also used for the preparation of other reference spinel supports (see the Supporting Information for details). All gold catalysts were prepared by the deposition-precipitation method with urea.[19] The surface area, mean AuNP size and Au loading of the catalysts are collected in Table 1. Under identical preparation conditions, all chromite spinels showed much lower surface area than aluminate spinels. The very low surface area of copper-containing chromite spinels is consistent with the presence of large crystals (see Figure S1, S2 for XRD patterns and SEM images). Evidently, the difference in spinel surface area has little influence on gold dispersion (Figure S3), with mean AuNP sizes always being between 2-4 nm.

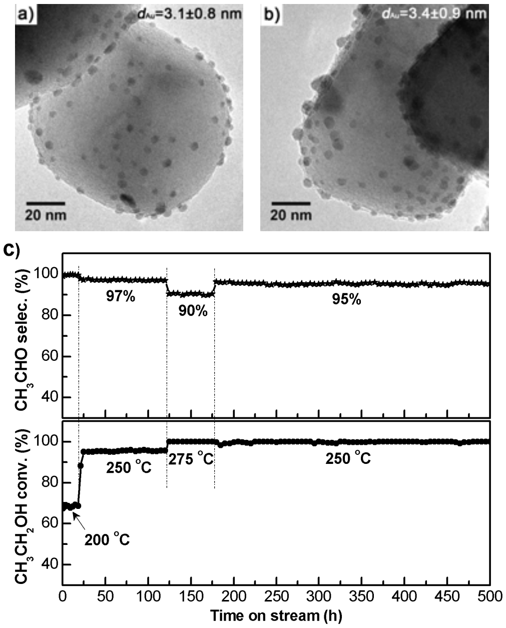

Figure 1. TEM images of a) fresh Au/MgCuCr$_2$O$_4$ catalyst, b) used Au/MgCuCr$_2$O$_4$ catalyst after 500 h on-stream; c) ethanol conversion and acetaldehyde selectivity vs time on stream using Au/MgCuCr$_2$O$_4$ (Reaction conditions: catalyst 0.1 g, GHSV = 100,000 mL g$_{cat}^{-1}$ h^{-1}, ethanol/O$_2$/He = 1/3/63).

Initially, we investigated the effect of the chromite-spinels on the catalytic activity of Au/MgMCr$_2$O$_4$ in gas-phase aerobic oxidation of ethanol (Table 1, entries 1-4). At 200 °C, acetaldehyde is the predominant product (selectivity > 95%) in all cases. Au/MgCuCr$_2$O$_4$ outperforms the other non-Cu containing catalysts (Table 1, entries 1-3) by nearly an order of magnitude, pointing to a strong synergy between AuNP and the Cu-containing spinel. To identify the beneficial effect of Cu-containing oxide supports, Au/CuCr$_2$O$_4$, Au/MgCuAl$_2$O$_4$ and Au/CuO-SiO$_2$ catalysts were also evaluated (Table 1, entries 5-7). These catalysts showed much lower activity than Au/MgCuCr$_2$O$_4$ catalyst, despite their higher Cu content, higher surface area and smaller AuNP size. Moreover, Au/MgCuCr$_2$O$_4$ also outperforms previously reported preferred Au/MgAl$_2$O$_4$,[7a] Au/SiO$_2$[10,11] and Au/TiO$_2$[12] catalysts for ethanol oxidation (Table 1, entries 8-10). These results clearly point to a specific gold-support interaction in the Au/MgCuCr$_2$O$_4$ catalyst.

Figure 2 shows the temperature dependence of ethanol conversion and acetaldehyde selectivity over representative catalysts. Au/MgCuCr$_2$O$_4$ exhibited higher activity than other catalysts below 300 °C, with a dramatic activity increase after 150 °C. The selectivity to acetaldehyde of Au/MgCuCr$_2$O$_4$ (see Table S1), interestingly, showed a maximum between 150-250 °C, with ethyl acetate as by-product at lower temperature and acetic acid and CO$_2$ as main by-products at higher temperature. Although Au/TiO$_2$ typically achieves moderate conversion at low temperature (~120 °C),[12] its performance is inferior to Au/MgCuCr$_2$O$_4$ at the same low temperature, mainly due to the much higher GHSV applied here (see Figure S4 for catalytic performance at lower GHSV). MgCr-spinel oxide supported AuNP (Au/MgCr$_2$O$_4$) without Cu showed low activity even at 300 °C, indicating the importance of Au-Cu interactions[16a]. Au/MgCuAl$_2$O$_4$ and Au/CuO-SiO$_2$ with much higher surface area and smaller AuNP size still showed inferior activity. These results further point to the pivotal role of the chromite-spinel support.

To investigate the stability of Au/MgCuCr$_2$O$_4$, the catalyst was run for 500 h in ethanol oxidation and the results are shown in Figure 1c. The catalyst was found to be stable at 200 °C for the first 20 h, and also at 250 °C for the following 100 h with conversion increasing to 95% and acetaldehyde selectivity slightly decreasing to 97%. When the temperature was further increased to 275 °C, full conversion was achieved during 50 h with selectivity decreasing to 90%. Interestingly, after decreasing the temperature to 250 °C, the conversion and selectivity remained at 100% and 95%, respectively, for more than 300 h. On the contrary, the ethanol conversion of Au/MgCuAl$_2$O$_4$ catalyst at 200 °C decreased from 30 to 25% after 5 h. To our delight, after 500 h on-stream, the structure and morphology of the Au/MgCuCr$_2$O$_4$ catalyst was largely retained (see Figure S2 for SEM image), with the average AuNP size only slightly increased from 3.1 to 3.4 nm (Figure 1a, 1b). Several other reference catalysts showed significant increases in the AuNP size after 50 h on-stream (see Figure S5), pointing to the stabilizing effect of MgCuCr$_2$O$_4$ on AuNP size. These results unequivocally demonstrate the highly efficient and robust nature of the Au/MgCuCr$_2$O$_4$ catalyst for the gas-phase ethanol oxidation to acetaldehyde. Considering that prior to reaction the catalyst was pre-treated in O$_2$ at 300 °C and the decreased activity for catalyst with larger AuNP size (Table 1, entry 11, also see Figure S6), we surmised that the activity increase may be due to ethanol-induced changes to the active sites.

Table 1. Textural and physicochemical properties and catalytic activity results for various supported Au catalysts.

	Catalyst	S_{BET} (m^2/g)	d_{Au} (*nm*)	[Au]^a (*wt*%)	X^b (%)	S^b (%)	TOF (h^{-1})^c
1	Au/MgCr$_2$O$_4$	16	3.3	0.93	6	96	207
2	Au/MgCoCr$_2$O$_4$	26	3.2	0.97	9	98	293
3	Au/MgNiCr$_2$O$_4$	17	3.3	0.96	7	96	233
4	Au/MgCuCr$_2$O$_4$	5	3.1	0.90	68	99	2351
5	Au/CuCr$_2$O$_4$	4	3.6	0.93	40	99	1556
6	Au/MgCuAl$_2$O$_4$	158	2.5	0.83	30	98	898
7^d	Au/CuO-SiO$_2$	165	2.8	0.93	20	97	592
8	Au/MgAl$_2$O$_4$	152	3.4	0.78	4	99	178
9^e	Au/SiO$_2$	287	6.3	1.87	12	92	378
10	Au/TiO$_2$	50	2.2	0.98	13	91	264
11^f	Au/MgCuCr$_2$O$_4$	5	4.5	0.90	38	99	1909
12^g	Au/MgCuCr$_2$O$_4$	5	3.1	0.90	73	99	2539

^{a} Determined by ICP-OES. ^{b} Ethanol conversion (X) and acetaldehyde selectivity (S) at 200 °C (catalyst 0.1 g, ethanol/O$_2$/He = 1/3/63, GHSV = 100,000 mL g$_{cat}^{-1}$ h^{-1}). ^{c} Turnover frequency based on acetaldehyde yield and gold dispersion (D = 1.3/d)^{11}, and given in mol$_{aldehyde}$ mol$_{surface\ Au}^{-1}$ h^{-1}. ^{d} By using CuO/SiO$_2$ (26.2 *wt*% Cu) as support. ^{e} By using Au(en)$_2$Cl$_3$ as precursor. ^{f} Catalyst was calcined at 500 °C in air for 5 h. ^{g} Pretreated in H$_2$ at 300 °C for 2 h.

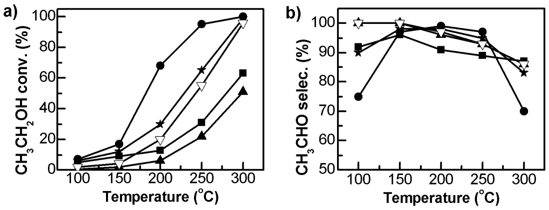

Figure 2. Temperature-dependent ethanol oxidation over various catalysts showing a) ethanol conversion, b) acetaldehyde selectivity. (●) Au/MgCuCr$_2$O$_4$, (★) Au/MgCuAl$_2$O$_4$, (■) Au/TiO$_2$, (▲) Au/MgCr$_2$O$_4$ and (▽) Au/CuO-SiO$_2$.

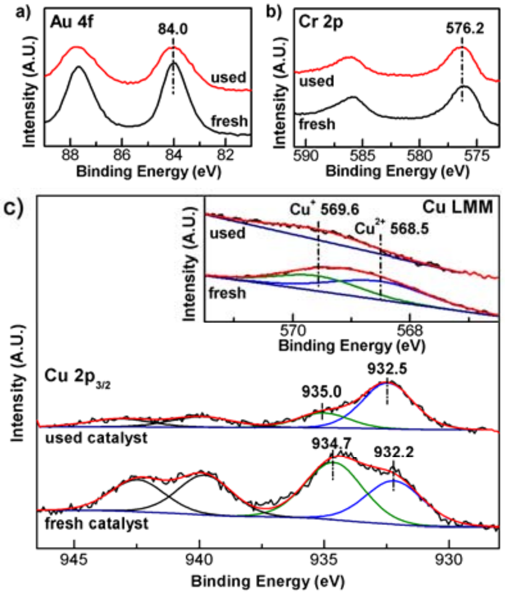

Figure 3. XP spectra of the Au/$MgCuCr_2O_4$ catalyst before and after 500 h on stream. a) Au 4f XP spectra, b) Cr 2p XP spectra, c) Cu $2p_{3/2}$ and Cu LMM (inset) XP spectra.

To obtain further insight into the gold-support interactions, we studied the oxidation state of Au, Cr and Cu of the fresh Au/$MgCuCr_2O_4$ catalyst and after catalyzing ethanol oxidation for 500 h by X-ray photoelectron spectroscopy (XPS, Figure 3). The binding energy (BE) was corrected for surface charging by taking the C 1s peak of contaminant carbon as a reference at 284.5 eV. The Au $4f_{7/2}$ BE remains constant at 84.0 eV, the value for metallic gold. Similarly, the BE of Cr $2p_{3/2}$ was ~576.2 eV, which is typically attributed to Cr^{3+}.[20] The Cu $2p_{3/2}$ XP spectra (Figure 3c) are different before and after use of Au/$MgCuCr_2O_4$ as a catalyst. Two contributions are discerned at 935 and 932 eV. The higher BE peak at ~935 eV is assigned to Cu^{2+} in the spinel, accompanied by the characteristic Cu^{2+} shake-up satellite peaks (938-945 eV).[21] The lower BE peak at ~932 eV suggests the presence of Cu^+ or Cu^0 species.[20,21] Because Cu $2p_{3/2}$ XPS cannot differentiate between Cu^+ and Cu^0, Auger Cu LMM spectra were used to confirm the presence of Cu^+ at BE ~570 eV.[22] This is consistent with the fact that both the spinel support and the gold catalyst were prepared by adopting a calcination step in air, so that the presence of metallic Cu in the fresh catalyst is not likely. Interestingly, significant changes were observed when comparing Cu XP spectra of the fresh and spent catalysts, with the Cu LMM transition showing only Cu^+ species. The surface Cu^+ fraction, derived from Cu $2p_{3/2}$ XP spectra, increased from 26 to 55% during 500 h time on stream, indicating that part of surface Cu^{2+} species are reduced to Cu^+ species during ethanol oxidation. To further prove the selective reduction of Cu^{2+} to Cu^+ in the $MgCuCr_2O_4$ spinel, the Au/$MgCuCr_2O_4$ catalyst and the $MgCuCr_2O_4$ support were pretreated in ethanol vapor or H_2 at 300 °C. XPS confirms the significantly increased surface Cu^+ content following these treatments and the absence of bulk Cu^0 species (see Figure S7). The surface Cu^+ fraction is 63% for H_2-reduced Au/$MgCuCr_2O_4$. The pre-reduced catalyst showed higher activity than the pre-oxidized one under identical conditions (Table 1, entry 12, also see Figure S8). These results further support that the synergy is related to the coexistence of Au^0 and Cu^+ species, and the increased catalytic performance at 250 °C after running for 50 h at 275 °C (Figure 1c) is due to enhanced Au^0-Cu^+ synergy. It is noteworthy that the surface Au/Cu atomic ratio in the pre-oxidized and pre-reduced Au/$MgCuCr_2O_4$ catalysts is similar (~0.7) and much higher than in the other Cu-containing catalysts (see Table S2). The somewhat decreased Au/Cu ratio (~0.6) in the spent catalyst after 500 h can be due to the small increase of AuNP size from 3.1 to 3.4 nm. These findings point to Au^0-Cu^+ interactions decreasing AuNPs sintering.

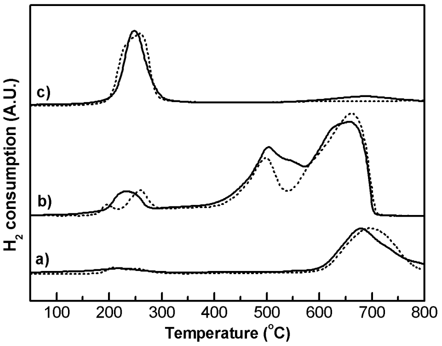

Figure 4. H_2 consumption traces (TPR) of a) Au/$MgCuCr_2O_4$, b) Au/$CuCr_2O_4$, and c) Au/$MgCuAl_2O_4$ catalysts. The dashed line represents the trace of the corresponding spinel support.

To understand the reducibility of the spinel supported gold catalysts, we performed temperature-programmed reduction (TPR) study (Figure 4). The amount of reducible species of the spinel supports and the gold catalysts derived thereof was found to be consistent with the Cu content (see Table S3). For the Au/$MgCuCr_2O_4$ and Au/$CuCr_2O_4$ catalysts, only 5.2 and 6.3% of the Cu species were reduced below 300 °C, respectively. In the case of Au/$MgCuAl_2O_4$, however, over 80% of Cu species was reduced below 300 °C, indicating the lower stability of Cu^{2+}/Cu^+ in the $MgCuAl_2O_4$ spinel. Although the surface Cu^+ fraction of fresh Au/$MgCuAl_2O_4$ catalyst is as high as 54%, the facile reduction of these Cu species to Cu^0 in the presence of ethanol (see Figure S9 for XPS results) results in inferior activity, presumably because of the absence of desirable Au^0-Cu^+ interactions. On the contrary, the Au/$MgCuCr_2O_4$ catalyst contains no Cu^0, demonstrating the advantage of $MgCr_2O_4$-type spinels in stabilizing Cu^{2+}/Cu^+ species. On the basis of these observations, the unique promotional effect of $MgCuCr_2O_4$ spinel support can be attributed to (i) the possibility of reducing Cu^{2+} to Cu^+ without Cu^0 formation, leading to development of Au^0-Cu^+ synergy beneficial for ethanol oxidation and, (ii) strong metal-support interactions, thus rendering robust Au/$MgCuCr_2O_4$ catalyst with stable AuNP size.

In an attempt to further understand the nature of Au^0-Cu^+ synergy and reaction mechanism, we determined the contribution of non-oxidative ethanol dehydrogenation to the total activity of aerobic ethanol oxidation. Indeed, $CuO{\cdot}CuCr_2O_4$ (copper chromite) is known to be an active catalyst for ethanol dehydrogenation.[23] Figure 5(a, b) shows the activity and selectivity comparison of $MgCuCr_2O_4$ spinel and Au/$MgCuCr_2O_4$ for ethanol conversion in the presence and absence of oxygen in the feed. Over the bare $MgCuCr_2O_4$ spinel, negligible oxidation took place at temperatures below 200 °C, but at higher temperature acetaldehyde was gradually produced accompanied by formation of ethyl acetate and CO_2 (see Table S4). The $MgCuCr_2O_4$ spinel, however, exhibited very poor activity for non-oxidative dehydrogenation of ethanol even at 350 °C, which we attribute to the absence of Cu^0 sites for the initial O-H bond cleavage in our catalyst.[24] Figure 5c shows that Au/$MgCuCr_2O_4$ deactivates during ethanol dehydrogenation and the more so at higher temperatures, with ethylene/ethyl acetate as main by-products. Compared with the excellent activity of Au/$MgCuCr_2O_4$ in aerobic oxidation, its low activity in dehydrogenation demonstrates the importance of O_2 for the Au^0-Cu^+ synergy. The absence of activated oxygen species as H acceptor to remove the surface adsorbed Au-H hydride and

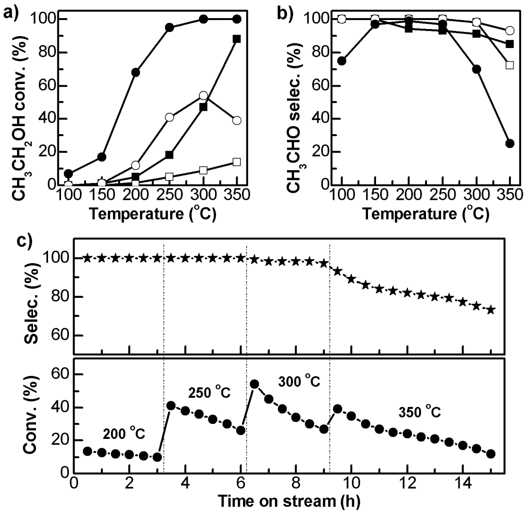

Figure 5. a) ethanol conversion, b) acetaldehyde selectivity for temperature-dependent aerobic oxidation of ethanol over (●) Au/$MgCuCr_2O_4$ and (■) $MgCuCr_2O_4$, and non-oxidative ethanol dehydrogenation over (○) Au/$MgCuCr_2O_4$ and (□) $MgCuCr_2O_4$; c) non-oxidative ethanol dehydrogenation performance vs time on stream using Au/$MgCuCr_2O_4$ (Reaction conditions: catalyst 0.1 g, GHSV = 100,000 mL g_{cat}^{-1} h^{-1}, ethanol/He = 1/66).

to release free Au^0 sites may be the reason for activity decreasing with the temperature and time increasing. XPS (see Figure S7) excludes the reduction of Cu^+ during non-oxidative ethanol dehydrogenation and temperature-programmed oxidation (TPO, Figure S10) confirms that rapid coking is the cause of the deactivation. On the contrary, in the presence of O_2, coking is suppressed and stable performance can be achieved.

Based on the above observations, we propose that O_2 activation occurs on Cu^+ sites instead of AuNP. This is supported by the finding that Au/$MgCr_2O_4$ is significantly less active for ethanol oxidation than Au/$MgCuCr_2O_4$. The resulting active oxygen species (O^- or O_2^-) are thought to act as basic sites to facilitate O-H bond cleavage and metal-alcoholate formation[6] (Scheme S1). AuNP in close proximity to such centers will act as the sites for C-H cleavage, which is believed to be the most difficult step in alcohol oxidation.[11,13a,15] We speculate that the oxidized Cu^{2+}-OH intermediates can be reduced by the proximate Au-H hydride formed by C-H cleavage of adsorbed Au-alcoholate, accompanied by water formation and removal, thereby recovering the initial Cu^+ and free Au^0 active centers. This novel synergistic effect between Cu^+ and Au provides a more efficient route for ethanol oxidation to acetaldehyde than using previously reported Cu^0-containing AuCu alloy catalysts.[15, 16a]

In summary, we report for the first time an approach to achieve highly efficient, selective and stable oxidation of ethanol to acetaldehyde by using $MgCuCr_2O_4$-spinel supported gold nanoparticles. This significant progress is based on the identification of a novel and potentially broader applicable Au-Cu synergy in alcohol oxidation, likely being based on the interaction of AuNPs with Cu^+ which activate O_2. The Cu^+ species are stabilized in a chromite-spinel phase and become more dominant at the surface during the ethanol oxidation. Through interactions with the Cu^+-containing chromite spinel the AuNPs are stable during reaction. We have already demonstrated stable ethanol oxidation operation at 250 °C (1.5 vol% ethanol and a GHSV of 100,000 mL g_{cat}^{-1} h^{-1}) for 500 h. Under these conditions, the ethanol conversion is complete and the acetaldehyde selectivity is 95%. It is therefore reasonable to state that the novel catalyst has potential for acetaldehyde production from bioethanol.

ASSOCIATED CONTENT

Supporting Information

Experimental details, preparation and characterization of the catalysts. These materials are available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

pliu503@hotmail.com; e.j.m.hensen@tue.nl

ACKNOWLEDGMENT

This research was financially supported by Programme Strategic Scientific Alliances between the Netherlands and China (Grant No. 2008DFB5-130). We thank the Cryo-TEM Research Unit of Eindhoven University of Technology for access to TEM facilities.

REFERENCES

(1) (a) Corma, A.; Iborra, S.; Velty, A. *Chem. Rev.* **2007**, *107*, 2411. (b) Alonso, D. M.; Bond, J. Q.; Dumesic, J. A. *Green Chem.* **2010**, *12*, 1493. (c) Gallezot, P. *Chem. Soc. Rev.* **2012**, *41*, 1538.

(2) (a) Rass-Hansen, J.; Falsig, H.; Jørgensen, B.; Christensen, C. H. *J. Chem. Technol. Biotechnol.* **2007**, *82*, 329. (b) Sun, J.; Zhu, K.; Gao, F.; Wang, C.; Liu, J.; Peden, C. H. F.; Wang, Y. *J. Am. Chem. Soc.* **2011**, *133*, 11096.

(3) Takei, T.; Iguchi, N.; Haruta, M. *Catal. Surv. Asia* **2011**, *15*, 80.

(4) Caro, C.; Thirunavukkarasu, K.; Anilkumar, M.; Shiju, N. R.; Rothenberg, G. *Adv. Synth. Catal.* **2012**, *354*, 1327.

(5) (a) Jira, R. *Angew. Chem. Int. Ed.* **2009**, *48*, 9034. (b) Keith, J. A.; Henry, P. M. *Angew. Chem. Int. Ed.* **2009**, *48*, 9038.

(6) (a) Hashmi, A. S. K.; Hutchings, G. J. *Angew. Chem. Int. Ed.* **2006**, *45*, 7896. (b) Pina, C. D.; Falletta, E.; Prati, L.; Rossi, M. *Chem. Soc. Rev.* **2008**, *37*, 2077. (c) Corma, A.; Garcia, H. *Chem. Soc. Rev.* **2008**, *37*, 2096. (d) Zhang, Y.; Cui, X.; Shi, F.; Deng, Y. *Chem. Rev.* **2012**, *112*, 2467.

(7) (a) Christensen, C. H.; Jørgensen, B.; Rass-Hansen, J.; Egeblad, K.; Madsen, R.; Klitgaard, S.; Hansen, S.; Hansen, M.; Andersen, H.; Riisager, A. *Angew. Chem. Int. Ed.* **2006**, *45*, 4648. (b) Jørgensen, B.; Christiansen, S. E.; Thomsen, M. L.; Christensen, C. H. *J. Catal.* **2007**, *251*, 332. (c) Tembe, S. M.; Patrick, G.; Scurrell, M. S. *Gold Bull.* **2009**, *42*, 321.

(8) Sun, K. Q.; Luo, S. W.; Xu, N.; Xu, B. Q. *Catal. Lett.* **2008**, *124*, 238.

(9) Biella, S.; Rossi, M. *Chem. Commun.* **2003**, 378.

(10) Zheng, N.; Stucky, G. D. *J. Am. Chem. Soc.* **2006**, *128*, 14278.

(11) Guan, Y.; Hensen, E. J. M. *Appl. Catal. A* **2009**, *361*, 49.

(12) (a) Simakova, O. A.; Sobolev, V. I.; Koltunov, K. Y.; Campo, B.; Leino, A.-R.; Kordás, K., Murzin, D. Y. *ChemCatChem* **2010**, *2*, 1535. (b) Sobolev, V. I.; Koltunov, K. Y.; Simakova, O. A.; Leino, A.-R.; Murzin, D. Y. *Appl. Catal. A* **2012**, *433-434*, 88.

(13) (a) Gong, J.; Mullins, C. B. *J. Am. Chem. Soc.* **2008**, *130*, 16458. (b) Kong, X. M.; Shen, L. L. *Catal. Commun.* **2012**, *24*, 34.

(14) Takei, T.; Iguchi, N.; Haruta, M. *New J. Chem.* **2011**, *35*, 2227.

(15) Bauer, J. C.; Veith, G. M.; Allard, L. F.; Oyola, Y.; Overbury, S. H.; Dai, S. *ACS Catal.* **2012**, *2*, 2537.

(16) (a) Pina, C. D.; Falletta, E.; Rossi, M. *J. Catal.* **2008**, *260*, 384. (b) Fan, J.; Dai, Y.; Li, Y.; Zheng, N.; Guo, J.; Yan, X.; Stucky, G. D. *J. Am. Chem. Soc.* **2009**, *131*, 15568.

(17) (a) Liu, P.; Guan, Y.; van Santen, R. A.; Li, C.; Hensen, E. J. M. *Chem. Commun.* **2011**, *47*, 11540. (b) Liu, P.; Li, C.; Hensen, E. J. M. *Chem. Eur. J.* **2012**, *18*, 12122.

(18) Sobczak, I.; Szrama, K.; Wojcieszak, R.; Gaigneaux, E. M.; Ziolek, M. *Catal. Today* **2012**, *187*, 48.

(19) Zanella, R.; Giorgio, S.; Henry, C. R.; Louis, C. *J. Phys. Chem. B* **2002**, *106*, 7634.

(20) Deutsch, K. L.; Shanks, B. H. *J. Catal.* **2012**, *285*, 235.

(21) Severino, F.; Brito, J. L.; Laine, J.; Fierro, J. L. G.; Agudo, A. L. *J. Catal.* **1998**, *177*, 82.

(22) Platzman, I.; Brener, R.; Haick, H.; Tannenbaum, R. *J. Phys. Chem. C* **2008**, *112*, 1101.

(23) Prasad, R. *Mater. Lett.* **2005**, *59*, 3945.

(24) Zhang, M.; Li, G.; Jiang, H.; Zhang, J. *Catal. Lett.* **2011**, *141*, 1104.

Table of content