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Aerobic oxidation of aqueous ethanol using heterogeneous gold catalysts: Efficient routes to acetic acid and ethyl acetate

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Abstract

The aerobic oxidation of aqueous ethanol to produce acetic acid and ethyl acetate was studied using heterogeneous gold catalysts. Comparing the performance of Au/$MgAl_2O_4$ and Au/TiO_2 showed that these two catalysts exhibited similar performance in the reaction. By proper selection of the reaction conditions, yields of 90–95% of acetic acid could be achieved at moderate temperatures and pressures. Based on our findings, a reaction pathway for the catalytic oxidation of ethanol via acetaldehyde to acetic acid is proposed, and the rate-determining step (RDS) in the mechanism is found to be the (possibly oxygen-assisted) dehydrogenation of ethanol to produce acetaldehyde. It also is concluded that most of the CO_2 formed as a byproduct in the reaction results from the absorbed intermediate in the dehydrogenation of ethanol to produce acetaldehyde. By varying the amount of water in the reaction mixture, the possibilities for producing ethyl acetate by the aerobic oxidation of ethanol is also studied. At low ethanol concentrations, the main product is acetic acid; at concentrations >60 wt%, it is ethyl acetate.

Keywords: Heterogeneous catalysis; Gold; Aerobic oxidation; Acetic acid; Ethyl acetate; Bioethanol

1. Introduction

Gold catalysis has attracted significant attention over the last two decades [1–4]. This increasing interest can be traced back primarily to two pioneering discoveries: the aerobic oxidation of CO and the addition of HCl to acetylene by Haruta et al. [5] and Hutchings et al. [6], respectively. Initially, it was primarily the possibility of performing preferential oxidation of carbon monoxide to carbon dioxide with dioxygen in the presence of dihydrogen that led to the growing interest in the special reactivity of supported nanosized gold particles [7,8]; however, most recently, the selective oxidation of alcohols to carbonyl compounds with dioxygen/air over gold catalysts has become of interest. Both supported gold particles and polymer-stabilized clusters have been investigated as possible catalysts for the selective oxidation of alcohols [9,10]. The substrates investigated to date include aromatic, aliphatic, and allylic alcohols; both primary and secondary alcohols; and some polyols. It has been suggested that aliphatic alcohols can be more difficult to oxidize than benzyllic alcohols [11]. For the polyols, gold catalysts have been reported to exhibit a higher chemoselectivity than the analogous supported palladium and ruthenium catalysts [12–14], thereby making it possible to control the alcohol group in the polyol that is preferentially oxidized. For the oxidation of aliphatic diols containing both a primary and a secondary alcohol group, the regioselectivity is highly shifted toward oxidation of the primary alcohol group [15]. In addition, the effect of the solvent is noteworthy, because in aqueous solution, the carboxylic acid is favored over the aldehyde, but in solvent-free experiments, aldehyde is favored [12]. Moreover, the use of Fe_2O_3 or C as a support material seems, in contrast to CeO_2-, TiO_2-, or SiO_2-supported catalyst, more active toward the formation of esters [16]. The group of Prati and Rossi investigated the oxidation of both simple alcohols and more complex polyols such as glucose [17–21]. They also studied in more detail the reactivity of various diols, particularly ethylene glycol

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and phenylethane-1,2-diol [15,22–25]. In these studies, it was found that the activity of gold on metal oxides increased with decreasing particle size, whereas for gold on carbon catalysts, the activity apparently reached a maximum at a mean diameter of 7–8 nm [22]. Hutchings et al. worked with both pure supported gold catalysts and Au/Pd alloys for the oxidation of alcohols and aldehydes [15,26]. Carrettin et al. studied the oxidation of glycerol in aqueous solution and found that oxidation occurred only in the presence of a base but still at moderate temperature (333 K) and with high selectivity [27,28]. Similarly, others also have conducted oxidation of glycerol with dioxygen using gold catalysts and found that the selectivity varied significantly with conversion [29]. Recently, Corma et al. used supported gold catalysts for the solvent-free oxidation of various alcohols and concluded that nanocrystalline CeO_2 acts as a co-catalyst, improving the catalytic activity of the gold [30]. They demonstrated that the gold catalyst is superior to palladium catalysts in the selective oxidation of secondary alcohols to form ketones [12], and also investigated the oxidation of allylic alcohols in detail [31]. In the case of the allylic alcohols, the gold catalyst was found to have significantly greater chemoselectivity than the Pd catalyst; moreover, gold makes it possible to form mainly the α,β-unsaturated carbonyl compound. Idriss et al. investigated the gas-phase oxidation of ethanol over an Au/CeO_2 catalyst in the temperature range of 373–1073 K and found that the product composition changed significantly with temperature [32]; at low temperatures, acetaldehyde was the main product, whereas at higher temperatures, the selectivity switched toward acetone and finally to methane.

Here we report the aerobic oxidation of one of the simplest alcohols, ethanol, using heterogeneous gold catalysts. Previously, we reported that using a $Au/MgAl_2O_4$ catalyst, high yields of acetic acid can be achieved when ethanol is oxidized in aqueous phase at moderate temperatures and pressures [33]. In this work, the influence of the support was been investigated and the reaction pathway clarified, with the origin of CO_2 as a side product in the reaction and the RDS identified. This could be important in improving the catalyst performance or for identifying completely new catalysts. Furthermore, we found that ethyl acetate also can be formed from ethanol solutions by aerobic oxidation.

The reason for specifically studying the oxidation of ethanol is that ethanol could be one of the future feedstocks of the chemical industry. Ethanol can be easily produced from agricultural products by fermentation and thus can be considered a renewable resource. The annual amount of bioethanol produced currently exceeds 50 million tons per year and is increasing. In comparison, the total amount of acetic acid produced annually is around 10 million tons. Thus, a sufficient amount of bioethanol is produced to have a significant impact, even if only part of it is used as a chemical feedstock rather than a fuel additive [34].

Crude bioethanol contains only 8–10 vol% ethanol [35], and thus purification of ethanol by distillation to produce a useful fuel is a very costly process. Consequently, an investigation aimed at determining whether crude bioethanol can be directly converted to acetic acid or ethyl ester, which could be less expensive to isolate industrially, is of great interest.

2. Experimental

All experiments were conducted in stirred Parr mini-reactor batch autoclaves, made of either T316 steel or titanium, with a total volume of 56 mL. First, 10 mL of the reagent mixture was transferred to the autoclave with 150 mg of the catalyst, after which the desired pressure of technical air was applied in the autoclave. The autoclave was heated under stirring and kept at the reaction temperature for the desired reaction time, then cooled in an ice bath to below 278 K. The liquid reaction mixture was analyzed on a Shimadzu GC-9A gas chromatograph equipped with a Nukol capillary column (15 m × 0.53 mm i.d., Supelco) and a flame ionization detector. The gas was collected in a gas sample bag and led into the sample loop of the Perkin–Elmer PE AutoSystem XL gas chromatograph equipped with a Porapak 80/100 mesh Supelco column and a thermal conductivity detector. The gas analyses were only done qualitatively, but the only gas-phase product detected was CO_2. Thus, the amount of CO_2 was calculated based on the carbon mass balance, because this was the only gaseous product of the reaction. The catalyst used for all experimental work (1.5% Au/TiO_2) was purchased from the World Gold Council and is a reference catalyst [36]. The catalyst was characterized by XRD, which showed that the TiO_2 support was phase-pure anatase. The pore volume and surface area were determined to be 0.507 and 45.6 m^2/g, respectively. The $Au/MgAl_2O_4$ catalyst was prepared as described previously [33]. A series of experiments with a 5 wt% solution of ethanol (1.09 M) was conducted to investigate both the time dependence and the temperature dependence of the formation of acetic acid and side products. Measurements were conducted in the temperature range of 363–473 K for time spans ranging from 15 min to 24 h. Furthermore, the catalyst was recycled several times to investigate the catalyst's lifetime/reusability.

To investigate which step in the oxidation of ethanol to acetic acid could be rate-limiting, experiments were conducted with a 5 wt% acetaldehyde solution at reaction times of 0.5–4 h. To further clarify the mechanism, experiments with aqueous solution of acetic acid also were conducted. All of the experiments designed to investigate the kinetics were conducted at 423 K and 3.5 MPa pressure.

For the ethyl ester formation, the reactions were run in several steps to achieve a sufficiently high oxygen content without going to pressures >3.5 MPa (at room temperature). This was done by first conducting one step as for the acetic acid formation and then quenching the autoclave to 273 K, with the depleted air let out. Then the autoclave was refilled with a new batch of air and the reaction was restarted. Several combinations of reaction times were investigated, but the best results were achieved when the reaction time of the first step was kept at 2 h and the second for four hours. The temperature was kept constant at 423 K for all of the experiments aimed at producing ethyl acetate. The ethanol concentration varied between 15 and 96 wt%.

Transmission electron microscopy images were obtained using a JEOL 3000 electron microscope. About 30 images were recorded for each catalyst sample.

3. Results and discussion

3.1. Acetic acid

Acetic acid is a commodity chemical that demonstrates relatively rapid growth in production volume and is used in several areas, including the production of vinyl acetate monomer, which is used for the manufacture of the polymer polyvinyl acetate. At present, the main route of acetic acid production is carbonylation of methanol [37]. This route uses fossil resources exclusively, with two separate steam-reforming steps usually involved in the process. We have previously shown that heterogeneous gold catalyst effectively facilitates the oxidation of ethanol to form acetic acid, which obviously represents a potential renewable route to acetic acid. In the present work, we studied this reaction in more detail.

We investigated the time dependency and temperature dependency of the reaction using the Au/TiO_2 catalyst under the same reaction conditions as reported for the Au/$MgAl_2O_4$ catalyst [33]. Our results show that the analogous experiments with the Au/TiO_2 catalyst gave very similar results. Fig. 1 shows temperature-dependent findings. When compared to our previous findings for Au/$MgAl_2O_4$ [33], the present results illustrate the catalysts' similar behaviors. Clearly, both the conversion and yield increased with increasing temperature; however, the two curves do not exhibit exactly the same form, providing a first indication that the reaction proceeds via an intermediate. For both catalysts, the yield of acetic acid reached >90% at high conversion; the level was slightly higher (95%) for the Au/TiO_2 catalyst than for the Au/$MgAl_2O_4$ catalyst, but the difference is close to the experimental uncertainty. This value corresponds to a space-time yield of about 0.24 mol/h/L.

Fig. 2 shows TEM images of the two catalysts demonstrating similar gold particle sizes (3–6 nm). However, on average, Au/TiO_2 has a slightly smaller particle size. Fig. 3 illustrates the effect of the reaction time on conversion and yield; it can be seen that at the given conditions, ethanol conversion increased with increased reaction time and finally reached >99%. The yield of acetic acid followed the same trend found for the Au/$MgAl_2O_4$ catalyst. Overall, the results demonstrate no significant difference between the two metal oxide supports; they do not exclude a possible influence of the support material on the catalyst activity, however. In particular, if the support were shifted to a non-metal oxide compound, the effect could be very different; this has been reported for the selective oxida-

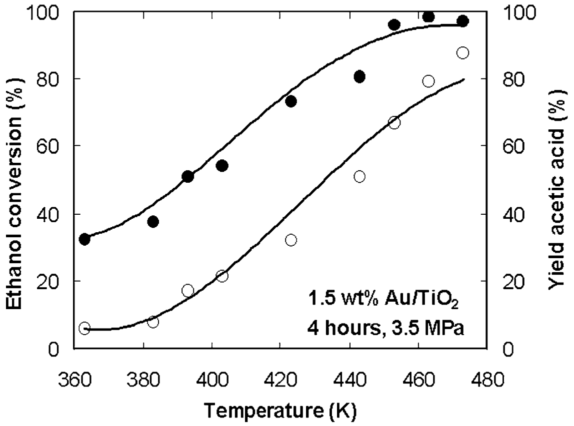


Fig. 1. Yield of acetic acid (○) and conversion of ethanol (●) as a function of temperature.

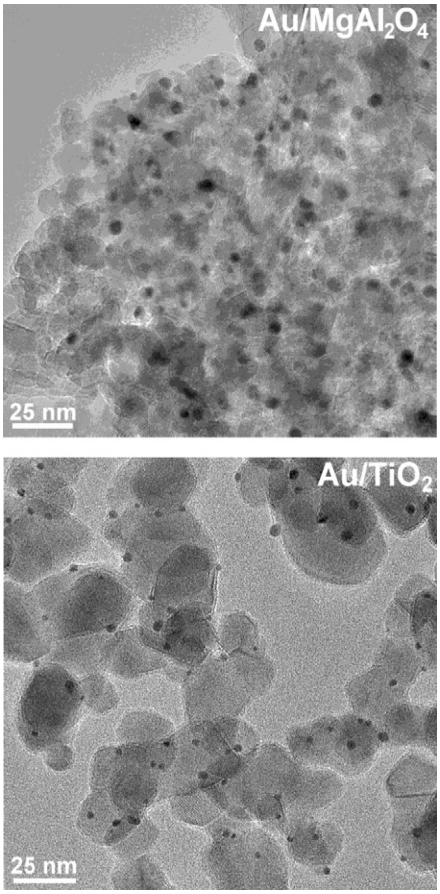


Fig. 2. TEM images of Au/$MgAl_2O_4$ (top) and Au/TiO_2 (bottom).

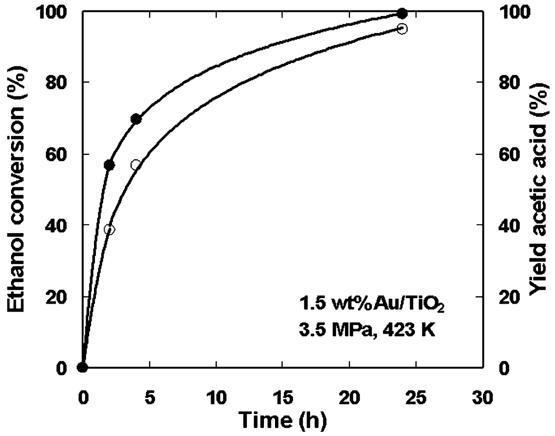


Fig. 3. Yield of acetic acid (○) and conversion of ethanol (●) as a function of time.

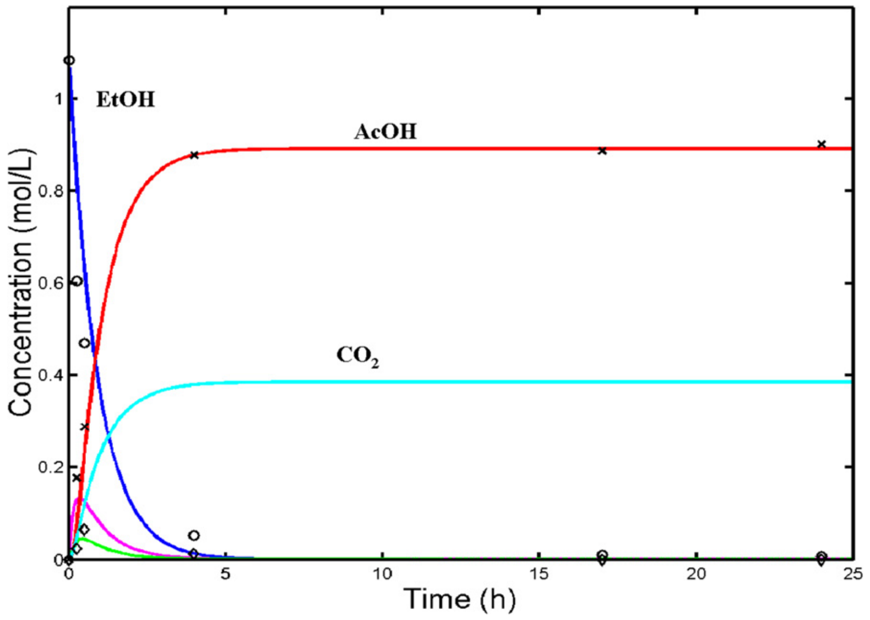


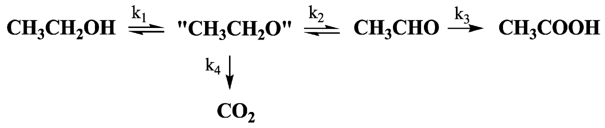
Fig. 4. Simple kinetic modeling of the reaction, solid lines theoretical values based on the reaction scheme in Fig. 5; (○, ×, ◇) experimental values (EtOH, AcOH, AcH). The green line represents acetaldehyde and the mauve the surface intermediate. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

tion of glucose [38]. Preliminary experiments using carbon as a support material have not demonstrated nearly as high conversion of ethanol or selectivity toward acetic acid as found for the present metal oxide supports. Experiments conducted with the pure support materials (TiO_2 and $MgAl_2O_4$) gave acetic acid yields $<2\%$.

The long-term stability of the TiO_2-supported catalyst did not seem to be better than that of the Au/$MgAl_2O_4$. A significant decrease in activity was seen when the catalyst was reused, but it remained active even after several runs. The used catalyst showed no signs of coke formation, as supported by its color. TEM images obtained from the catalyst maintained under reaction conditions for 10 days clearly showed that the gold particle size increased significantly but remained <10 nm. Typical particle sizes in the spent catalyst were around 5–7 nm. Small alterations of the catalyst composition might possibly improve the long-term stability. Along these lines, Mirescu et al. [38] recently studied gold catalysts with quite long lifetimes, but under much milder reaction conditions than those that we used, where the catalyst was subjected to hydrothermal conditions.

3.2. *Kinetics*

Studying the reaction in more detail as a function of the reaction time revealed that not only acetic acid, but also acetaldehyde as well as CO_2 were formed. Moreover, a very small amount of ethyl acetate also was detected when the ethanol concentration was increased slightly. Our results demonstrate that acetaldehyde was formed in higher concentrations when the reaction time was kept short, as shown in Fig. 4. This figure clearly indicates that the reaction proceeded via acetaldehyde before forming acetic acid. To determine the RDS, an aqueous solution of acetaldehyde was used as the reagent instead of the ethanol solution. These experiments showed that the RDS



$$\begin{tikzcd} CH_3CH_2OH \arrow[r, shift left, "k_1"] & \text{"}CH_3CH_2O\text{"} \arrow[l, shift left] \arrow[r, shift left, "k_2"] \arrow[d, "k_4"'] & CH_3CHO \arrow[l, shift left] \arrow[r, "k_3"] & CH_3COOH \\ & CO_2 & & \end{tikzcd}$$

Fig. 5. Reaction pathway, “CH_3CH_2O” is the dehydrogenation intermediate.

most likely was the dehydrogenation of ethanol, because the oxidation of acetaldehyde occurred very rapidly. The CO_2 formation detected can be presumed to originate from full oxidation of an adsorbed reaction intermediate. This supposition is supported by experimental data showing that acetic acid did not decompose to form CO_2; in fact, the acetic acid concentration remained constant after 24 h. Furthermore, experiments with acetaldehyde gave 100% conversion and an acetic acid yield of at least 98%, indicating that the aldehyde was not decomposed exclusively to CO_2. This finding is in agreement with others investigators, who have proposed a similar reaction pathway for the same reaction using another catalyst [39]. The simple kinetic model in Fig. 5 explains all of these observations.

Consequently, we propose the reaction pathway shown in Fig. 5. In this pathway, ethanol is first adsorbed to the catalyst surface, where an activated intermediate species is formed, which then is oxidized/dehydrogenated to the aldehyde. Finally, the aldehyde is further oxidized to the acid. The intermediate, CH_3CH_2O, can undergo C–C bond cleavage to produce CO_2 or can lead to the formation of acetaldehyde.

The given model can be fitted quite well to the experimental data given in Fig. 4, achieving the values for the rate constants displayed in Table 1. The difference in the values for the rate constants k_2 and k_4 can be explained by the fact that the full oxidation of the intermediate (k_4) involves C–C bond-breaking, whereas dehydrogenation (k_2) requires only C–H bond-breaking, which is less demanding. Furthermore, the RDS

Table 1
Fitted values of first-order rate constants (mol/(L h))

Rate constant	k_1	k_2	k_3	k_4
Value	1.1	5.1	14.1	1.1

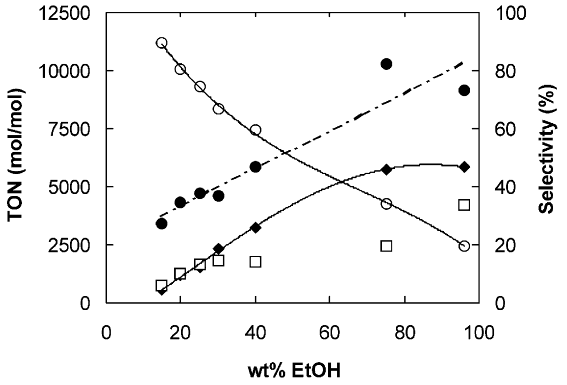


Fig. 6. Selectivity and activity of the gold catalyst as a function of the concentration of ethanol (○, acetic acid; ◆, ethyl acetate; □, acetaldehyde; ●, TON).

for the formation of acetic acid obviously is related to the activation of the ethanol (k_1). This step involves the (possibly oxygen-assisted) dehydrogenation of ethanol to form acetaldehyde.

3.3. *Ethyl acetate*

Ethyl acetate is typically produced by esterfication of acetic acid. It has a wide range of applications in, for instance, the paint industry and also is gaining interest as a substitute for methyl ethyl ketone in, for example, the food industry [40]. Previously, methyl esters have been produced by gold-catalyzed oxidation of a methanolic solution of primary alcohol using oxygen as the oxidant both with and without the presence of base [14,41]. Similarly, Corma et al. [30] reported that aliphatic primary alcohols can be oxidized to the corresponding ester. Nonetheless, ester formation in aqueous solutions has not yet been investigated in detail.

Consequently, we have explored the possibility of forming ethyl ester by making small alterations to the reaction conditions used for the production of acetic acid. Increasing the ethanol concentration increased the selectivity toward ethyl acetate, as expected. However, when the concentration was <60 wt% ethanol, the major product remained acetic acid. Fig. 6 plots the selectivity in the liquid phase as well as the turnover number (TON) as a function of ethanol concentration. The selectivities are based on the mol of products (EtOAc, AcOH, and AcH) in the liquid phase. Fig. 6 clearly shows a decrease in selectivity toward acetic acid and a concomitant increase in selectivity toward the ethyl ester. However, the selectivity toward the ester appeared to reach a maximum at the highest concentrations. The concentration of acetaldehyde, the major remaining product, increased at lower water content. Under the reaction conditions used here, ethanol conversion decreased due to the oxygen deficiency imposed by use of relatively low dioxygen pressure and reaction time, which were kept constant for all concentrations; however, the TON increased with increasing concentration, indicating that the catalyst remained active even at the high ethanol concentrations.

Under the given reaction conditions, the acetic acid-to-ethyl acetate ratio was determined largely by thermodynamic constraints. Thus, ethyl acetate formation was limited by the water content in the reaction mixture, because water obviously participates in the equilibrium for the ester formation. The water content is determined not only by the amount of water present in the feed, but also by the extent of the reaction and by the selectivity. In particular, a significant amount of water is formed when CO_2 is produced. Thus, using crude bioethanol for such an ethyl acetate process requires using a feed with a low water content, which adds to the cost of the feedstock. In addition, the importance of a highly selective catalyst is clear.

4. Conclusion

Aerobic oxidation of ethanol over a heterogeneous gold catalyst has been found to be slightly dependent on whether spinel or titania is used as the support material, with the latter giving the highest yields. Furthermore, a reaction mechanism has been postulated for the conversion of ethanol to acetic acid going through two intermediates, one unknown and the other acetaldehyde, and with only one significant byproduct, CO_2. The RDS was found to be the dehydrogenation of the ethanol to form acetaldehyde; this might be a two-step process, with a supported intermediate converted to acetaldehyde. This simple kinetic model was supported by the experimental data.

The reaction conditions were modified to seek a higher selectivity toward the ethyl ester. This was achieved by altering the ethanol concentration. At low ethanol concentration, the major product was acetic acid, but at higher concentrations, the selectivity was shifted toward ethyl acetate, as expected. However, concentrations >60 wt% were needed, indicating that water had a significant limiting effect.

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References

[1] G.J. Hutchings, M. Haruta, Appl. Catal. A 291 (2005) 2.
[2] M. Haruta, M. Daté, Appl. Catal. A 222 (2001) 427.
[3] D. Thompson, Gold Bull. 31 (1998) 111.
[4] D. Thompson, Gold Bull. 32 (1999) 12.
[5] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet, B. Delman, J. Catal. 144 (1993) 175.
[6] B. Nkosi, N.J. Coville, G.J. Hutchings, M.D. Adams, J. Friedl, F.E. Wagner, J. Catal. 128 (1991) 366.
[7] T.V.W. Janssens, B.S. Clausen, B.H. Larsen, H. Falsig, C.H. Christensen, T. Bligaard, J.K. Nørskov, Top. Catal. 44 (2007) 15.
[8] M. Haruta, Gold Bull. 37 (2004) 27.
[9] H. Tsunoyama, H. Sakurai, Y. Negishi, T. Tsukuda, J. Am. Chem. Soc. 127 (2005) 9374.

[10] H. Tsunoyama, H. Sakurai, T. Tsukuda, Chem. Phys. Lett. 429 (2006) 528.
[11] A. Biffis, L. Minati, J. Catal. 236 (2005) 405.
[12] A. Abad, D. Almela, A. Corma, H. García, Tetrahedron 62 (2006) 6666.
[13] M. Besson, P. Gallezot, Catal. Today 57 (2000) 127.
[14] T. Hayashi, T. Inagaki, N. Itayama, H. Baba, Catal. Today 117 (2006) 210.
[15] S. Biella, L. Prati, M. Rossi, Inorg. Chim. Acta 349 (2003) 253.
[16] D.I. Enache, D.W. Knight, G.J. Hutchings, Catal. Lett. 103 (2005) 43.
[17] S. Biella, L. Prati, M. Rossi, J. Catal. 206 (2002) 242.
[18] S. Biella, L. Prati, M. Rossi, J. Mol. Catal. A 197 (2003) 207.
[19] S. Biella, M. Rossi, Chem. Commun. (2003) 378.
[20] M. Comotti, C.D. Pina, R. Matarrese, M. Rossi, A. Siani, Appl. Catal. A 291 (2005) 204.
[21] L. Prati, F. Porta, Appl. Catal. A 291 (2005) 199.
[22] C. Bianchi, F. Porta, L. Prati, M. Rossi, Top. Catal. 13 (2000) 231.
[23] F. Porta, L. Prati, M. Rossi, G. Scari, J. Catal. 211 (2002) 464.
[24] L. Prati, M. Rossi, J. Catal. 176 (1998) 552.
[25] L. Prati, G. Martra, Gold Bull. 32 (1999) 96.
[26] D.I. Enache, J.K. Edwards, P. Landon, B. Solsona-Espriu, A.F. Carley, A.A. Herzing, M. Watanabe, C.J. Kiely, D. W Knight, G.J. Hutchings, Science 311 (2006) 362.
[27] S. Carrettin, P. McMorn, P. Johnston, K. Griffin, C.J. Kiely, G.J. Hutchings, Phys. Chem. Chem. Phys. 5 (2003) 1329.
[28] S. Carrettin, P. McMorn, P. Johnston, K. Griffin, G.J. Hutchings, Chem. Commun. (2002) 696.
[29] N. Dimitratos, A. Villa, C.L. Bianchi, L. Prati, M. Makkee, Appl. Catal. A 311 (2006) 185.
[30] A. Abad, P. Concepción, A. Corma, H. Garcia, Angew. Chem. Int. Ed. 44 (2005) 4066.
[31] A. Abad, C. Almela, A. Corma, H. García, Chem. Commun. (2006) 3178.
[32] P.-Y. Sheng, G.A. Bowmaker, H. Idriss, Appl. Catal. A 261 (2004) 171.
[33] C.H. Christensen, B. Jørgensen, J. Rass-Hansen, K. Egeblad, R. Madsen, S.K. Klitgaard, S.M. Hansen, M.R. Hansen, H.C. Andersen, A. Riisager, Angew. Chem. Int. Ed. 45 (2006) 4648.
[34] J. Rass-Hansen, H. Falsig, B. Jørgensen, C.H. Christensen, J. Chem. Technol. Biotechnol. 82 (2007) 329.
[35] W. Soetaert, E. Vandamme, in: P. Lens, P. Westermann, M. Haberbauer, A. Moreno (Eds.), Biofuels for Fuel Cells, IWA Publishing, London, 2005, p. 37.
[36] http://www.gold.org/discover/sci_indu/gold_catalysts/refcat.html.
[37] N. Yoneda, S. Kusano, M. Yasui, P. Pujado, S. Wilcher, Appl. Catal. A 221 (2001) 253.
[38] A. Mirescu, H. Berndt, A. Martin, U. Prüße, Appl. Catal. A 317 (2007) 204.
[39] E. Iglesia, personal communication, 2007.
[40] R. Sakamuri, Esters, Organic in Kirk-Othmer Encyclopedia of Chemical Technology, online version on Wiley InterScience.
[41] I.S. Nielsen, E. Taarning, K. Egeblad, R. Madsen, C.H. Christensen, Catal. Lett. 116 (2007) 35.