Catalysis Today 154 (2010) 7–12

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Hydrogen from formic acid decomposition over Pd and Au catalysts

Dmitri A. Bulushev[a,b], Sergey Beloshapkin[b], Julian R.H. Ross[a,*]

[a] *Charles Parsons Initiative, Chemical & Environmental Sciences Department, University of Limerick, Limerick, Ireland*
[b] *Materials & Surface Science Institute, University of Limerick, Limerick, Ireland*

ARTICLE INFO

Keywords:
HCOOH decomposition
Hydrogen
Palladium
Gold
Catalytic transfer hydrogenation
Water–gas shift reaction

ABSTRACT

Vapour phase decomposition of formic acid has been studied systematically over a range of catalysts: 1.0 and 10 wt.% Pd/C, 0.8 wt.% Au/C and 1.0 wt.% Au/TiO_2. The mean metal particle size of these materials was estimated by HRTEM and turnover frequencies were calculated using these data. The Au/C catalyst was the least active and the Pd/C catalysts were the most active for the formic acid decomposition reaction. At about 400 K, these Pd catalysts gave up to 0.04 moles of H_2 per minute per gram of Pd, with a selectivity of 95–99%. The H_2 selectivity for these catalysts was found to be only weakly dependent on the reaction temperature and the formic acid conversion. The Au/TiO_2 catalyst showed only a moderate selectivity to H_2 formation (<70%). The selectivity of this catalyst was improved considerably by the introduction of water vapour. This improvement derived from the high activity of the catalyst for the water–gas shift reaction.

1. Introduction

The decomposition of formic acid has long been used as a test reaction to distinguish between catalysts favouring dehydrogenation (Eq. (1)) and those favouring dehydration (Eq. (2)):

$$HCOOH \rightarrow CO_2 + H_2 \qquad (1)$$

$$HCOOH \rightarrow CO + H_2O \qquad (2)$$

The first reaction is slightly exothermic while the second is slightly endothermic. The selectivity to H_2 and CO_2 can be determined either kinetically or thermodynamically; in the latter case, the water–gas shift (WGS) reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (3)$$

is in equilibrium and increased H_2 selectivity is favoured by lower temperatures.

Fahrenfort et al. [1] examined the decomposition of formic acid over different metal catalysts and correlated the data with the heats of formation of the corresponding bulk metal formates. A volcano shaped dependence was obtained, with Pt and Ir as the most active catalysts, these being followed by Pd, Ru and Ir. They found that gold was only weakly active in the decomposition reaction. It is now clear that catalysts containing finely dispersed gold can be much more active in a variety of different catalytic reactions than can bulk metallic gold [2–4]. Ojeda and Iglesia [5] have very recently shown that the turnover frequencies for the decomposition of formic acid over catalysts supported on alumina and containing gold nanoparticles with mean sizes in the range 3–5 nm could be significantly higher than those containing platinum nanoparticles; in both cases, the selectivity for hydrogen production was close to unity.

Iglesia and Boudart [6,7] studied the decomposition of formic acid using Cu, Ni and Ni/Cu catalysts and found that the selectivities for hydrogen production were 0.75–0.83 for the Ni and Ni-rich catalysts and 0.95–0.98 for the Cu and Cu-rich catalysts. They reported for the Cu catalysts that the turnover frequency for formic acid decomposition was independent of the concentrations of the decomposition products (CO, CO_2, H_2), the metal loading, the metal dispersion and the nature of the support (Al_2O_3, SiO_2). Solymosi and Erdohelyi have performed a detailed study of the same reaction over Rh catalysts on different supports [8]. They found that the selectivities were high, 0.86, 0.9 and 0.95 for Rh on Al_2O_3, MgO and SiO_2, respectively, and moderate, 0.63–0.7, for Rh on TiO_2. They reported that the reaction order was equal to one and suggested that the adsorption of formic acid was the rate determining step for the Rh catalysts.

There are several reasons for a renewal of interest in the catalytic decomposition of formic acid:

(i) formic acid is obtained in high concentrations as a by-product (until now, undesirable and of no significant value) in some second generation biorefinery processes [9];
(ii) formic acid can be used effectively as a fuel in fuel cells [10–13];
(iii) formic acid can be used as a hydrogen donor in catalytic transfer hydrogenation reactions [14,15].

---

* Corresponding author. Tel.: +353 61202641; fax: +353 61202734.
E-mail address: julian.ross@ul.ie (J.R.H. Ross).

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.03.050

Generally, Ni and Cu catalysts have been studied in formic acid decomposition in more detail than have Pd and Au catalysts. We have reported previously that a series of supported metal alloy catalysts containing 5 wt.% Pd gave good conversions of formic acid vapour together with high selectivities towards hydrogen and CO_2 in the temperature range 473–573 K [16]. Zhou et al. have recently shown that Pd/Au and Pd/Ag alloys supported on activated carbon are effective for the decomposition of aqueous solutions of formic acid containing sodium formate at low temperature (ca. 365 K) [11]. The objective of the present work was to examine the factors determining the activity of Pd and Au catalysts in the vapour phase decomposition of formic acid and to determine the suitability of these materials for hydrogen production; the catalysts used were in almost all cases supported on carbon but one gold catalyst supported on titania was also examined for comparative purposes.

2. Experimental

The Pd catalysts used in these studies, samples of 10 wt.% Pd/C (Degussa type, E101 NE/W) and 1 wt.% Pd/C, were provided by Sigma–Aldrich. Two samples of gold catalysts, 1 wt.% Au/TiO_2 and 0.8 wt.% Au/C, were supplied by the World Gold Council. Full characterisation of these Au-containing catalysts and information about their preparation can be found elsewhere [17,18].

TEM measurements were carried out on a JEM-2011 (JEOL) electron microscope operated at 200 kV. The dispersion of the Pd particles was calculated from the number-averaged mean particle sizes; the sizes of more than a hundred particles were measured for each sample.

For the catalytic experiments reported here, 6.8 mg (dry weight) of a 10 wt.% Pd/C sample was diluted with quartz grains to give a total bed weight of 0.26 g, this being placed in a quartz tubular reactor of 4 mm internal diameter. For the 1 wt.% Pd/C, 1 wt.% Au/TiO_2 and 0.8 wt.% Au/C samples, the weights used were 60, 69 and 85 mg, respectively. The samples were reduced in a 1 vol.% H_2/Ar mixture at 573 K for 1 h and cooled in He to the reaction temperature. An equivalent reductive pretreatment of the catalysts was performed before their transfer in air to the transmission electron microscope.

The catalytic experiments were carried out in a flow reactor system which was constructed in such a way that it was possible to bring about a rapid change of the composition of the reaction mixtures flowing over the catalyst without there being any change in the total gas flow rate or the initial formic acid concentration. Formic acid (Riedel-de Haan, 98–100% purity) was introduced into an evaporation volume using a syringe-pump (Sage); the system lines through which it flowed were heated to 340 K to prevent condensation. Helium was used as a carrier gas for all the experiments with formic acid. Enrichment of the gas mixture with water vapour could be achieved if necessary by passing He through a vessel containing liquid water. A standard hydrogen–argon mixture (1 vol.% H_2/Ar) and the individual components of various experimental mixtures (He, H_2, CO_2) were supplied by BOC Gases and were introduced to the system via mass-flow controllers. The WGS reaction (Eq. (3)) was tested with a gas mixture of the following composition: 2.3 vol.% CO, 2.3 vol.% H_2O, balance He. The majority of the experiments (except those examining the dependence of the conversion on contact time or the reaction orders) were performed with a total flow rate of 51 cm^3 (STP) min^{-1}. The reactants and products were analysed by a gas chromatograph (HP-5890) fitted with a Porapak-Q column and a TCD detector. No methanol or methane formation was observed in any of the experiments carried out.

The formic acid conversions reported here are given as the ratios of the sum of CO and CO_2 concentrations in the products to the initial concentration of formic acid. The CO_2 selectivity is given as the ratio of the CO_2 concentration to the sum of the CO and CO_2 concentrations. For the reactions (1) and (2), the selectivity to CO_2 also corresponds to the hydrogen selectivity. The hydrogen yield for any set of conditions was calculated by multiplying the selectivity by the conversion. The turnover frequency values (TOF) were determined as the ratio of the rate of hydrogen formation from formic acid to the number of surface metal sites, determined from TEM data.

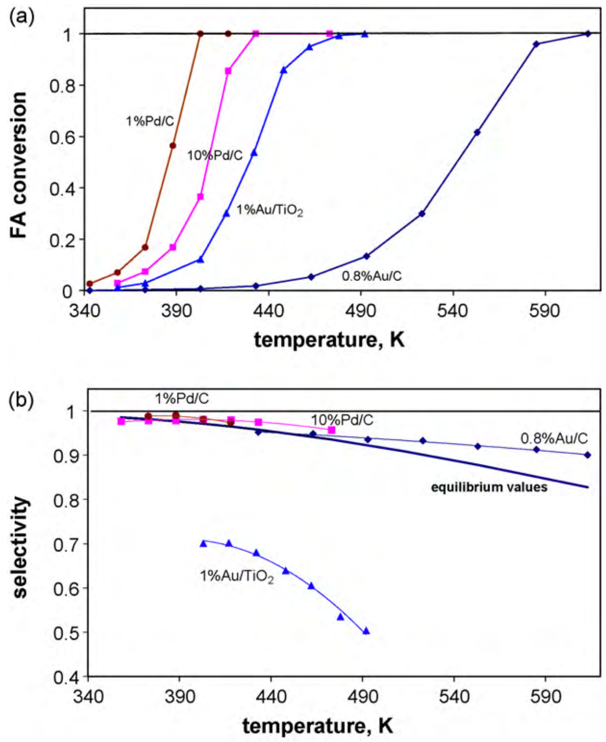

Fig. 1. Temperature dependences of (a) the steady-state conversions and (b) H_2 selectivity obtained during the HCOOH decomposition (2.4 vol.% HCOOH/He) over the 1 wt.% Pd/C, 10 wt.% Pd/C, 1 wt.% Au/TiO_2 and 0.8 wt.% Au/C catalysts taken with charges of 60, 6.8, 69 and 85 mg, respectively. The WGS reaction equilibrium values are shown for comparison.

3. Results and discussion

3.1. Catalytic properties

Fig. 1(a) shows the steady-state conversions of formic acid found in the decomposition reaction over the different catalysts using approximately the same active metal charge for each sample. It was found that the Pd/C catalysts were the most active of the samples studied. Complete conversion was reached at about 390 K with the 1 wt.% Pd/C sample. The rate of hydrogen formation for this sample was as high as 0.04 moles of H_2 per minute per gram of Pd under the conditions used. The catalyst sample containing 1 wt.% of Pd was found to be more active in terms of rate per unit weight of metal than was that with 10 wt.%. This was a result of the higher dispersion of Pd in the sample with the lower Pd content. Table 1 shows the mean Pd particle sizes and dispersions of the different Pd/C catalysts, these having been calculated from the particles size distributions shown in Fig. 2. The dispersion of Pd in the 1 wt.% Pd/C sample was 1.5 times higher than that in the 10 wt.% Pd/C sample and the particles size distribution was much narrower. Generally, the Pd particles were spherical in shape. The concentrations of surface Pd atoms in the samples were calculated from the TEM particle size data (Table 1) using the equation presented in reference [19] and these values were used to calculate the values of the turnover frequency (TOF) for each sample.

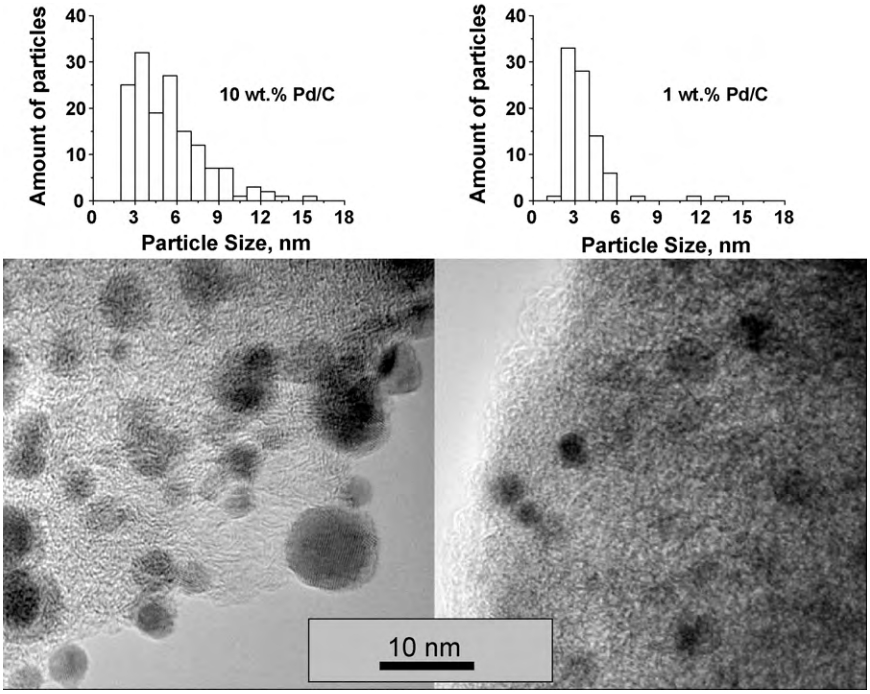

Fig. 2. TEM pictures and particles size distributions of the pre-reduced 10 wt.% Pd/C and 1 wt.% Pd/C catalysts.

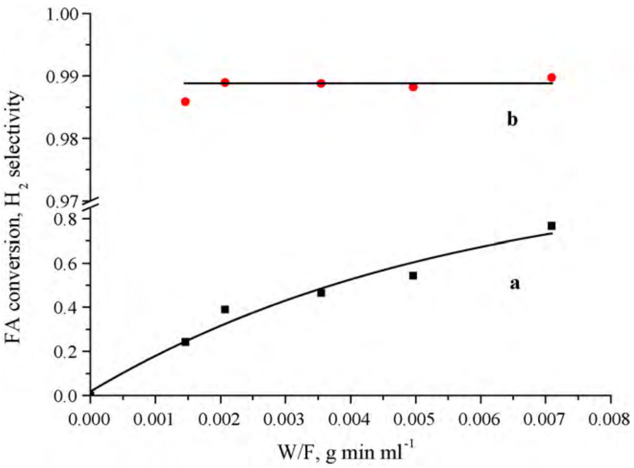

Fig. 3. Dependence of (a) HCOOH conversion and (b) H_2 selectivity on contact time obtained for HCOOH decomposition over the 10 wt.% Pd/C catalyst (6.8 mg) at 403 K (2.4 vol.% HCOOH/He). W, catalyst weight; F, HCOOH flow rate.

The activities of the Au/C catalyst at various temperatures were low (Fig. 1(a)) compared with those of the Au/TiO_2 sample; however, both samples were significantly less active than the Pd catalysts. It is known that a synergism occurs between Au nanoparticles and titania that this gives rise to samples with significant activities for various different reactions [2,20]. This synergism also appears to apply to the formic acid decomposition reaction studied here.

The selectivity to hydrogen was very high for all the Pd catalysts, with values in the range 0.97–0.99 at low reaction temperatures (Fig. 1(b)). The value of the selectivity for each of the samples was only weakly dependent on the temperature used, decreasing slightly to a value of 0.95 at about 473 K. Fig. 3 demonstrates a dependence of the conversion and selectivity on the contact time at 403 K. The conversion behaviour (Fig. 3(a)) is determined by the reaction kinetics, these involving inhibition by products as discussed later. The selectivity was found to be almost independent of the contact time and of the conversion of the formic acid (Fig. 3(b)). This could indicate that the dehydration and dehydrogenation reactions of formic acid take place in parallel. The contribution of the WGS reaction under these conditions seems to be negligible. Nevertheless, making the assumption that the WGS reaction equilibrium (Eq. (3)) occurred, equilibrium values of the selectivity, S, were calculated for different temperatures using Eq. (4) to make comparisons:

$$S = \frac{1}{(1 + 1/\sqrt{K})} \tag{4}$$

where K is the equilibrium constant of the WGS reaction. Eq. (4) can easily be derived by using the equations for the selectivity and the equilibrium constant, taking into account the fact that during formic acid decomposition the concentration of hydrogen is equal to the concentration of carbon dioxide and that the concentration of water is equal to the concentration of carbon monoxide. The value

Table 1
BET surface areas, mean particle sizes determined by TEM, dispersion, concentrations of surface metal sites, turnover frequencies for H_2 production from HCOOH (TOF_{H_2}) activation energies (E_a) and pre-exponential factors (A).

Catalysts	BET surface area ($m^2\ g^{-1}$)	Mean particle size (nm)	Dispersion	Concentration of surface metal sites ($\times10^{-21}$ per gram of metal)	TOF_{H_2} at 373 K (s^{-1})	E_a (kJ mol^{-1})	A ($\times10^{-7}\ s^{-1}$)
1 wt.% Pd/C	760	3.6	0.31	1.8	0.071	65	9.7
10 wt.% Pd/C	950	5.4	0.21	1.2	0.050	67	12.8
1 wt.% Au/TiO_2	50 [18]	3.5 [17]	0.33	1.0	0.016	63	1.3
0.8 wt.% Au/C	1200 [18]	10.5 [17]	0.11	0.34	0.006	55	0.014

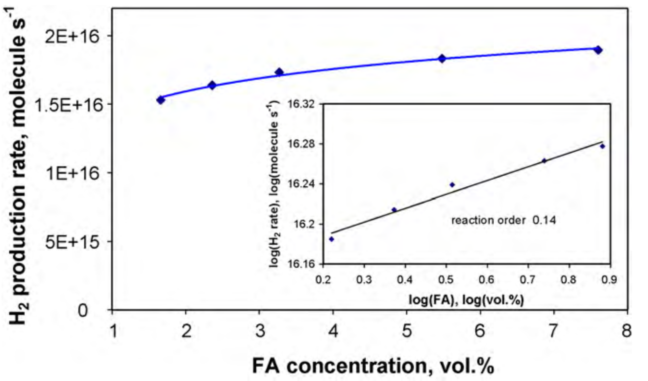

Fig. 4. Dependence of H_2 production rate on the concentration of HCOOH; and (inset) reaction order determination for HCOOH decomposition (2.4 vol.% HCOOH/He) over the 10 wt.% Pd/C catalyst (6.8 mg) at 358 K.

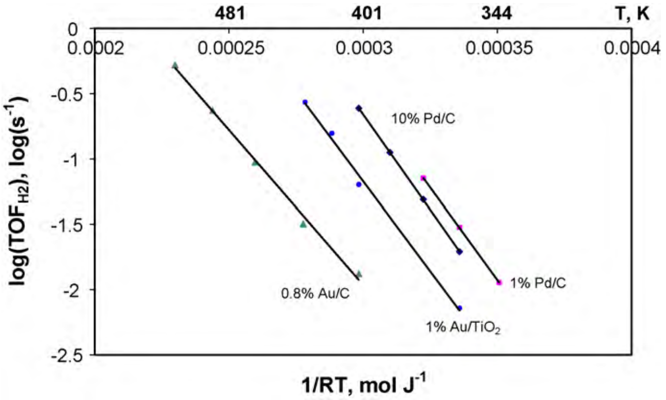

Fig. 5. Arrhenius plots of turnover frequencies for H_2 production from HCOOH (2.4 vol.% HCOOH/He).

of K was determined using Eq. (5) [21]:

$$K = \exp\left(\frac{4577.8}{T} - 4.33\right) \tag{5}$$

The resultant values of the selectivity are shown in Fig. 1(b) where they are compared with the experimental data. It can be seen that the experimental selectivities are equal to, or slightly greater than, the equilibrium values for both carbon-supported Pd catalysts and the Au/C catalyst; the values of the selectivity were slightly lower for the Au/C catalyst than for the Pd/C catalysts. In contrast, the selectivities for the Au/TiO_2 catalyst were much lower (<0.70). As was reported earlier [15], the hydrogen yield for this catalyst did not exceed 0.6 while the hydrogen yields for all carbon-supported catalysts could be higher than 0.9. Solymosi and Erdohelyi have also found lower H_2 selectivities in the formic acid decomposition reaction for Rh/TiO_2 catalysts than with Rh/Al_2O_3, Rh/MgO and Rh/SiO_2 catalysts [8]. It is known that pure titania leads to formic acid decomposition with a selectivity only in the direction of CO and H_2O formation (dehydration) [8,22]. The lower selectivities observed for the catalysts supported on titania compared with the other catalysts examined may be related to the participation of the titania support in the reaction.

The rates of hydrogen production as a function of the concentration of formic acid in the range from 1.7 to 7.6 vol.% were determined at low conversions and the results are shown in Fig. 4. Under these conditions, the concentrations of the products in the reaction mixture were approximately constant. This was achieved by varying the He flow rate while keeping a constant formic acid flow. As CO and H_2 may inhibit formic acid decomposition over the Pd/C catalysts at low temperatures (see later), the inhibiting effect of products is an important constraint. The dependence of the rate on the formic acid concentration shown in Fig. 4 was very weak and the apparent reaction order was found to be very low, 0.14 (Fig. 4, inset). A zero order dependence was reported earlier by other authors for Cu [6], Ni [1] and Au [5] catalysts. Such dependence is consistent with the decomposition of the surface formate species probably being rate determining. Solymosi et al. suggested that formate species are unstable intermediates in the formic acid decomposition reaction on a Pd surface [23]. Davis and Barteau showed that surface formate species decomposed in vacuum on Pd monocrystals at low temperatures (280 K) giving mainly CO_2 and adsorbed hydrogen [24]. We suggest that under the conditions of the experiments reported here, high concentrations of formic acid and temperatures about 373 K, the Pd sites are covered by formate species which then decompose to give the products.

TOFs for hydrogen production were calculated from the catalytic results of Fig. 1(a) and (b) using the TEM data to give an estimate of the concentration of surface metal sites. The results are shown in Table 1 and are plotted in Fig. 5 as Arrhenius plots. All the Pd catalysts had quite similar TOFs in spite of a factor of 1.5 times difference in the dispersion. The TOFs obtained for the Pd catalysts were 1–2 orders of magnitude higher than those which have been reported for Cu [6], Ni [7] and Rh [8] catalysts for experiments under quite similar conditions. However, the values were lower than those reported by Ojeda and Iglesia [5] for dispersed Au/Al_2O_3 catalysts. The TOFs were also lower than those found for the liquid phase decomposition of formic acid over Ru complexes containing phosphine ligands [12].

All the values for the activation energies found for hydrogen production from formic acid were in the range 55–67 kJ mol^{-1} (Table 1). Similar activation energies have been reported for well dispersed Au/Al_2O_3 catalysts [5]. However, the values were much lower than those reported for Cu and Ni catalysts (100 kJ mol^{-1}) [6,7] and were only slightly lower than those reported for Rh catalysts (69–84 kJ mol^{-1}) [8].

The TOFs of the Pd/C catalysts were about one order of magnitude higher than those of the Au/C catalyst (Fig. 5 and Table 1). However, the activation energy for this gold catalyst was even lower (55 kJ mol^{-1}) than that for Pd (65–67 kJ mol^{-1}). Hence, the difference comes largely from differences in the pre-exponential factors (Table 1). This might be an indication that only a limited proportion of the surface gold atoms are active in the decomposition of the formic acid. Gold atoms with low coordination on Au nanoparticles are thought to be very active in catalytic reactions such as CO oxidation [25]. It has also been suggested that very small gold clusters which are invisible using TEM may be the active sites [5]. A decrease in the mean particle size may lead to an increase of the concentration of these active atoms. The higher TOFs for formic acid decomposition to give hydrogen over the Au/TiO_2 catalyst than those for the Au/C catalyst are in accordance with this consideration (Table 1).

3.2. Effects of products on catalytic activity

Catalytic biomass conversion processes give rise to products containing significant quantities of water together with valuable organic products. This water should not poison the catalysts used in subsequent reactions. The effects of water vapour on the conversion of formic acid and selectivity were studied in attempt to increase hydrogen yields by encouraging the WGS reaction to take place. As shown in Fig. 6, although water gave little change in formic acid conversion over the Au/TiO_2 catalyst, a significant improvement in the selectivity to hydrogen was found after water addition to the feed: the selectivity increased from 0.68 to 0.95. The latter value is quite close to the value expected if the WGS reaction is in

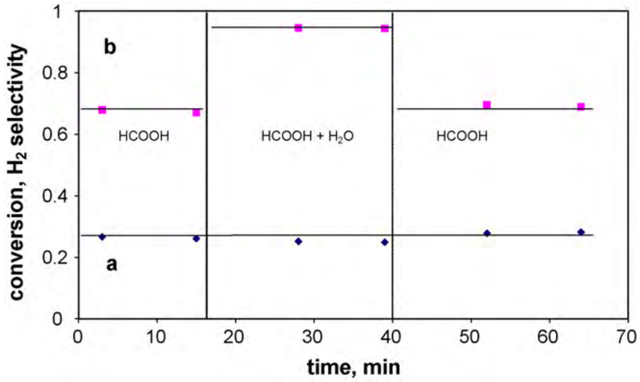

Fig. 6. The effect of added water vapour on (a) the HCOOH conversion and (b) the H_2 selectivity for HCOOH decomposition over the 1 wt.% Au/TiO_2 catalyst (69 mg) at 418 K. (Compositions: 2.4 vol.% HCOOH or 2.4 vol.% HCOOH/2.3 vol.% H_2O balance He.)

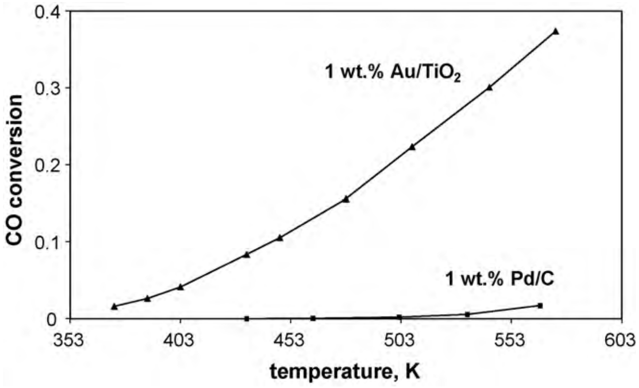

Fig. 7. Conversions of CO in the water–gas shift reaction over 1 wt.% Au/TiO_2 (69 mg) and 1 wt.% Pd/C (60 mg) catalysts as a function of reaction temperature (2.3 vol.% CO, 2.3 vol.% H_2O balance He).

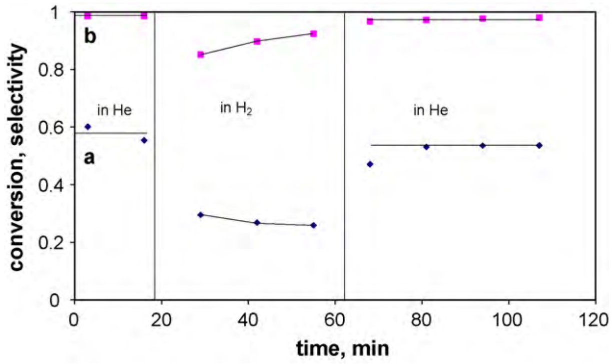

Fig. 8. The effect of hydrogen on (a) the conversion of HCOOH and (b) the selectivity to CO_2. Catalyst 6.8 mg of 10 wt.% Pd/C; temperature 405 K; gaseous composition 2.4 vol.% HCOOH, balance He or H_2.

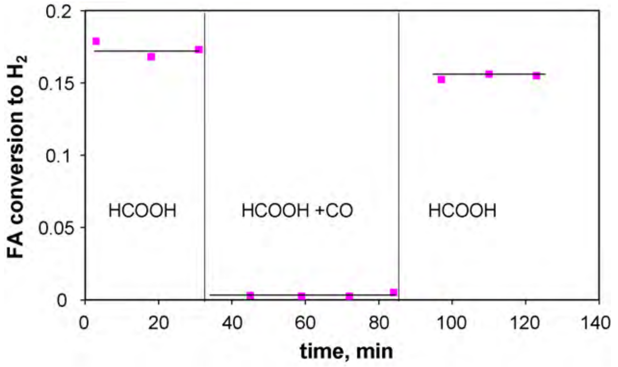

Fig. 9. The effect of CO (2.3 vol.%) on the HCOOH conversion to hydrogen obtained during HCOOH decomposition (2.4 vol.% HCOOH/He) over the 10 wt.% Pd/C catalyst (6.8 mg) at 383 K.

equilibrium (Fig. 1(b)). This improvement is related to the ability of the Au/TiO_2 catalyst to bring about the WGS reaction, as shown by the results depicted in Fig. 7. It is seen that a measurable conversion of CO in the WGS reaction over the Au/TiO_2 catalyst could be observed even at quite low temperatures (<373 K) as compared to the Pd/C catalyst for which it was only seen at temperatures 150 K higher. This high activity was in accordance with the activity of other Au/TiO_2 systems [20].

A limited effect of water on the decomposition of formic acid over the 10 wt.% Pd/C catalyst has previously been reported by us [15]. This effect was much less pronounced than for the Au/TiO_2 sample (Fig. 6): the conversion increases by only 10% and the selectivity seems to increase also, but negligibly. The lower effect with the Pd/C sample could occur because of a lower rate for the reaction of adsorbed CO with water vapour to give the WGS reaction products, with the liberation of active sites for formic acid decomposition. This is consistent with the observation that the WGS reaction was much slower over the Pd/C catalyst than over the Au/TiO_2 catalyst (Fig. 7). However, the hydrogen selectivity for the Pd catalyst was very high, even without water addition (Fig. 1(b)).

Fig. 8 shows the results of an experiment when helium in the reaction mixture was substituted by hydrogen. Hydrogen was found to give a significant decrease of the activity as well as a noticeable decrease of the selectivity. The effect was reversible: substitution of the hydrogen by helium once more led to the initial values of conversion and selectivity. It is known that hydrogen is adsorbed reversibly on Pd at the temperatures used here and it seems that such adsorption blocks the surface sites active for the formic acid decomposition. Earlier, we reported a similar hydrogen effect at much lower hydrogen concentrations [15]. A similar effect of added hydrogen has previously been observed for Rh containing catalysts [8]; however, Rh gave some methane formation, in contrast to Pd with which no methane was observed under any conditions. It is possible that methane and/or methanol may also be formed on Pd catalysts at higher temperatures and pressures [26].

The effect of CO addition was also studied. In the experiments presented in Fig. 9, the helium of the reaction mixture was rapidly substituted by a 2.5 vol.% CO/He mixture and then this mixture was in turn substituted by helium alone. The effect of CO was more significant than the effect of hydrogen reported above (Fig. 8). The formic acid decomposition was almost completely inhibited by CO at 383 K. It is known that CO adsorption on a Pd surface is quite strong and that the adsorption is almost irreversible at temperatures lower than 323 K. In this case, the adsorption seems to block the sites needed for formic acid decomposition. A similar effect of CO has been observed in the decomposition of formic acid in the liquid phase over Pd/C catalysts [11] as well as in the vapour phase decomposition of formic acid over Ni [7] and Rh [8] catalysts. In contrast to the results for the Pd catalysts, we did not find any effect of CO during the decomposition of formic acid over the Au/TiO_2 catalyst at 418 K. A similar lack of inhibition has been reported for Cu catalysts [6] and these results are consistent with the well-established weaker adsorption of CO on gold and copper. In contrast to the effect of CO, we found no effect of CO_2 during formic acid decomposition over the Pd/C catalyst. In these experiments helium was substituted by a 4 vol.%/CO_2/He mixture at 388 K. The absence of an effect of CO_2 on formic acid decomposition has also previously been reported for Ni [7] and Rh [8] catalysts.

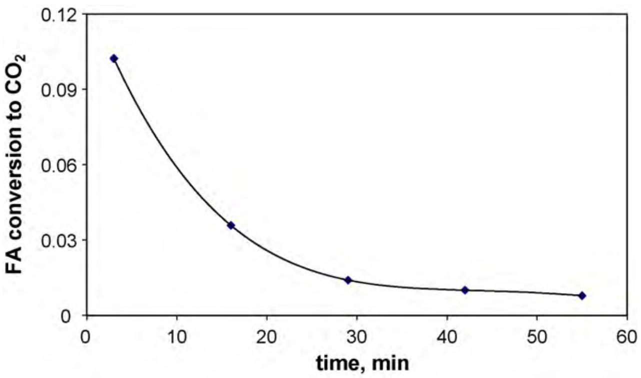

Fig. 10. Conversion–time dependence obtained during HCOOH decomposition (2.4 vol.% HCOOH/He) over the 1 wt.% Pd/C catalyst (60 mg) at 318 K.

As CO and H_2 are formed during the formic acid decomposition, it could be expected that their accumulation on the surface after formic acid introduction may lead to a decrease of the formic acid conversion with time. In accordance with this expectation, a substantial deactivation with time was found during the decomposition of formic acid over the 1 wt.% Pd/C catalyst at a relatively low temperature (318 K, see Fig. 10). This behaviour was not observed at temperatures higher than 373 K when the steady state equilibration between adsorbed and gaseous products was quickly installed. Thus, the inhibition effect at lower temperatures was assigned to slow formation of adsorbed CO and hydrogen from formic acid; once formed, they appear to compete with formic acid for the active Pd sites.

4. Conclusions

Pd/C catalysts were found to be quite active for the decomposition of formic acid at low temperatures (<400 K) giving hydrogen with selectivities of 0.95–0.99. The selectivities were only weakly dependent on the reaction temperature and the formic acid conversion. The formic acid decomposition rates were also only weakly dependent on the formic acid concentration (1.7–7.6 vol.%). Inhibition by adsorbed CO and H_2 could be extremely important if the reaction was performed in a closed system at low temperatures. Adsorbed CO and hydrogen strongly affect the kinetics of formic acid decomposition over Pd catalysts under these conditions.

The activity of the Au/C catalyst was very low. The Au/TiO_2 catalyst, in contrast to the Pd catalysts, was found to be resistant to CO poisoning. However, the addition of water vapour was necessary to achieve a high selectivity to hydrogen comparable with that of the Pd catalysts. This gold catalyst was found very active in the WGS reaction. The results obtained could be useful for the development of fuel cells and of hydrogen transfer hydrogenation processes.

Acknowledgements

This publication has emanated from research conducted with the financial support of Science Foundation Ireland under Grant Number 06/CP/E007.

References

[1] J. Fahrenfort, L.L. van Reyen, W.M.H. Sachtler, in: J.H. de Boer (Ed.), Proceedings of the Symposium on the Mechanism of Heterogeneous Catalysis, Elsevier, Amsterdam/London/New York/Princeton, 1960, p. 23.
[2] G.C. Bond, D.T. Thomson, Catal. Rev.-Sci. Eng. 41 (1999) 319.
[3] M. Haruta, Catal. Today 36 (1997) 153.
[4] D.A. Bulushev, I. Yuranov, E.I. Suvorova, P.A. Buffat, L. Kiwi-Minsker, J. Catal. 224 (2004) 8.
[5] M. Ojeda, E. Iglesia, Angew. Chem.-Int. Ed. 48 (2009) 4800.
[6] E. Iglesia, M. Boudart, J. Catal. 81 (1983) 214.
[7] E. Iglesia, M. Boudart, J. Catal. 81 (1983) 224.
[8] F. Solymosi, A. Erdohelyi, J. Catal. 91 (1985) 327.
[9] D.J. Hayes, S. Fitzpatrick, M.H.B. Hayes, J.R.H. Ross, in: B. Kamm, P.R. Gruber, M. Kamm (Eds.), Biorefineries—Industrial Processes and Products, vol. 1, Wiley–VCH, Weinheim, 2006, p. 139.
[10] S. Ha, R. Larsen, R.I. Masel, J. Power Sources 144 (2005) 28.
[11] X.C. Zhou, Y.J. Huang, W. Xing, C.P. Liu, J.H. Liao, T.H. Lu, J. Chem. Soc. Chem. Commun. (2008) 3540.
[12] S. Enthaler, Chemsuschem 1 (2008) 801.
[13] C. Fellay, P.J. Dyson, G. Laurenczy, Angew. Chem.-Int. Ed. 47 (2008) 3966.
[14] R.A.W. Johnstone, A.H. Wilby, I.D. Entwistle, Chem. Rev. 85 (1985) 129.
[15] D.A. Bulushev, J.R.H. Ross, Catal. Today, in press, doi:10.1016/j.cattod.2010.01.055.
[16] A. Ersson, K. Persson, S. Jaras, J.R.H. Ross, Abstr. Papers Am. Chem. Soc. 231 (2006).
[17] E. Taarning, A.T. Madsen, J.M. Marchetti, K. Egeblad, C.H. Christensen, Green Chem. 10 (2008) 408.
[18] P. Lignier, F. Morfin, L. Piccolo, J.L. Rousset, V. Caps, Catal. Today 122 (2007) 284.
[19] T. Lear, R. Marshall, J.A. Lopez-Sanchez, S.D. Jackson, T.M. Klapotke, M. Baumer, G. Rupprechter, H.J. Freund, D. Lennon, J. Chem. Phys. 123 (2005) 174706.
[20] H. Sakurai, A. Ueda, T. Kobayashi, M. Haruta, J. Chem. Soc. Chem. Commun. (1997) 271.
[21] J.M. Moe, Chem. Eng. Progr. 58 (1962) 33.
[22] M.A. Henderson, J. Phys. Chem. B 101 (1997) 221.
[23] F. Solymosi, A. Erdohelyi, M. Lancz, J. Catal. 95 (1985) 567.
[24] L. Davis, M.A. Barteau, Surf. Sci. 256 (1991) 50.
[25] N. Lopez, T.V.W. Janssens, B.S. Clausen, Y. Xu, M. Mavrikakis, T. Bligaard, J.K. Norskov, J. Catal. 223 (2004) 232.
[26] G.C. Cabilla, A.L. Bonivardi, M.A. Baltanas, Appl. Catal. A 255 (2003) 181.