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Vapour phase hydrogenation of olefins by formic acid over a Pd/C catalyst

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ABSTRACT

It has been found that ethylene and propylene could be effectively hydrogenated by formic acid vapour over a Pd/carbon catalyst at low temperatures ($<$440 K). Surface hydrogen formation from formic acid is the rate-determining step for this hydrogenation reaction. Interaction of this hydrogen with the olefins is then fast. The conversion of formic acid in the presence of either of the olefins at any temperature is higher than in their absence. This has been explained by a much lower surface hydrogen concentration in the presence of the olefins. Direct experiments have confirmed that hydrogen inhibits the formic acid decomposition. Water vapour addition has a small positive effect on the decomposition of formic acid as well as on the hydrogenation of the olefins with formic acid. Catalysts consisting of gold supported on carbon or titania are both active in the production of hydrogen from formic acid. However, in contrast to the Pd/C catalyst, neither gives hydrogenation of the olefins with this acid.

1. Introduction

There is currently significant interest in the development of “second generation” biorefineries, an example being the Biofine Process; this process transforms non-food biomass feedstock by acid catalysed hydrolysis to give an equimolar mixture of levulinic acid and formic acid together with some furfural and a “char” residue [1]. The levulinic acid can be used for the production of chemicals and transport fuel additives. We are currently examining potential uses of the formic acid fraction. For example, formic acid can be catalytically decomposed to give hydrogen and CO_2 (dehydrogenation):

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

A parallel reaction (dehydration) gives water and CO:

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

The selectivity to H_2 and CO_2 in formic acid decomposition can be determined either kinetically or thermodynamically; in the latter case, the water-gas shift reaction:

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

is in equilibrium and hence a high CO_2 selectivity is favoured by lower temperatures. A catalyst giving high selectivities to hydrogen and CO_2 is desirable since any CO formed will act as a catalyst poison if the hydrogen is to be used, for example, in a fuel cell [2].

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)) [3]. We have reported previously that a number of alloy catalysts containing palladium and supported on alumina give good conversions of formic acid vapour with high selectivities towards hydrogen and CO_2 at relatively low temperatures [4]. Zhou et al. have recently reported that Pd/Au and Pd/Ag alloys supported on carbon are also effective at low temperature (ca. 365 K) for the decomposition of aqueous solutions of formic acid containing sodium formate [5].

An important application of formic acid could be catalytic transfer hydrogenation reactions utilising formic acid as a source of hydrogen. A significant contribution to studies of this type of reaction has been made between 1952 and 1960 by Braude and Linstead [6,7]. These reactions have been reviewed by Brieger and Nestrick [8] and more recently by Johnstone et al. [9]. The hydrogen transfer reactions generally occur between relatively large organic molecules in the liquid phase and the catalysts studied have been predominantly homogeneous. Conventional hydrogenation catalysts such as supported Pd or Raney Ni can also be applied for such reactions. An example of such work is that by Nishiguchi et al. [10] who showed that Pd supported on carbon (or asbestos) and unsupported Pd-black could catalyse the transfer of hydrogen from various organic compounds to give hydrogenation of cycloheptene; the most reactive donor compound was indoline and this was followed in descending activity by formic acid, tetrahydroquinoline, piperidine and a range of other hydrogen-donating molecules. In a

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recent paper in which hydrogen transfer from formic acid occurs in a gas phase system, Glinski et al. [11] showed that carboxylic acids may be reduced to the corresponding aldehydes using formic acid over alumina-supported Mn, Ce and Zr oxides at temperatures above 573 K.

Catalytic hydrogen transfer reactions could be of industrial importance as the transportation and storage of hydrogen donors can be cheaper than those for molecular hydrogen. There could also be selectivity, activity, safety and energy benefits. Hydrogen transfer reactions may have some importance for conversion of biomass intermediates into fuel additives. In a recent patent to the Shell Oil Company [12] it has been shown, that using formic acid as a hydrogen donor levulinic acid and ethyl levulinate could be catalytically converted into γ-valerolactone, an excellent gasoline additive [13]; Ni/Pt and Re/Pt supported on silica as well as Cu/Cr oxide are mentioned among the catalysts. Additionally, it has recently been demonstrated that the same reactions could be performed using some homogeneous and heterogeneous Ru catalysts [14,15]. It has also been reported that formic acid may play an important role in the conversion of biomass lignin into aromatic compounds [16].

The majority of publications dealing with hydrogen transfer reactions of this type discuss the possibility of hydrogenating different organic compounds over a range of catalysts without demonstrating a deep understanding of the processes taking place or of their dependence on the concentrations of reactants and products, the temperature and the catalyst composition. Further, we have found no mention in the earlier publications of the possibility of hydrogenating ethylene and propylene by formic acid in vapour phase. We have now shown that gaseous formic acid can be used as a source of hydrogen for hydrogenation of simple olefins such as ethylene and propylene:

$$HCOOH + C_2H_4 \rightarrow CO_2 + C_2H_6 \qquad (4)$$

when Pd supported on carbon is used as catalyst and that the formation of CO is negligible under these conditions. A detailed study of these simple reactions may provide a deeper understanding of the processes which would occur in more complicated hydrogenation reactions.

It has recently been shown that supported gold catalysts can be active in catalytic transfer reduction of carbonyl compounds by isopropanol to give the corresponding alcohols [17]. To determine whether gold catalysts can also be used in formic acid reactions, experiments were carried out to examine the use of two different gold catalysts for the hydrogenation of olefins by formic acid and also for formic acid decomposition and the results are also given in this paper.

2. Experimental

A sample of 10 wt.% Pd/C (Sigma–Aldrich, Degussa type, E101 NE/W) with the BET surface area of 760 $m^2 g^{-1}$ was used as catalyst. The mean Pd particle diameter determined by transmission electron microscopy (TEM) was found to be 5.4 nm. Two gold catalyst samples, 1 wt.% Au/TiO_2 and 0.8 wt.% Au/C, were supplied by the World Gold Council and were thoroughly described elsewhere [18,19]. The BET surface areas for these samples were reported to be 50 and 1200 $m^2 g^{-1}$, respectively, and the mean metal particles diameters determined by TEM were 3.5 and 10.5 nm.

For the experiments reported here, a 6.8-mg (dry weight) sample of the Pd/C catalyst 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. The amount of the gold catalysts placed into the reactor corresponded to the same active metal charge taken for the 10 wt.% Pd/C catalyst and corresponded to 69 and 85 mg for the Au/TiO_2 and Au/C, respectively. The samples were reduced in a 1 vol.% H_2/Ar mixture at 573 K for 1 h and then cooled in He to reaction temperature. The reaction system used included a combination of three- and four-way valves and mass-flow controllers arranged in such a way as to permit a rapid change of the reaction mixtures flowing over the catalyst without a change in the total gas-flow rate (51 ml (STP)/min) or the initial formic acid concentration (2.4 vol.% in He). The formic acid (Riedel – de Haan, 98–100% purity) was introduced into an evaporation volume using a syringe-pump (Sage) at a rate to give this concentration; the system lines through which it flowed were heated to 340 K to prevent condensation. Saturation of the gas mixture with water vapour was achieved by passing He through a vessel containing liquid water maintained at 291 K. The pure gases or gas mixtures used to make up the reaction mixture (He, H_2, CO_2, 1 vol.% H_2/Ar, 2.5 vol.% CO/He, 1 vol.% C_2H_4/He and 1 vol.% C_3H_6/He) were introduced via mass-flow controllers. The olefin/He mixtures used were supplied by Air Products while the other gases were supplied by BOC Gases.

The forward and reverse water-gas shift reactions were tested using gas mixtures with the following compositions: 2.3 vol.% CO, 2.3 vol.% H_2O, balance He; and 20 vol.% CO_2, 20 vol.% H_2, balance He. The hydrogenation of the olefins with molecular hydrogen was tested with mixtures of 0.5 vol.% of the olefin with 0.5 vol.% H_2, the balance being He. The catalyst charges and total flow rates used were the same as those used for the formic acid decomposition studies.

The reaction products were analysed by a gas chromatograph (HP-5890) fitted with a Porapak-Q column and a TCD detector. The detection limit for CO in any gas mixture was about 15 ppm. Neither methanol nor methane formation was observed in the experiments carried out. The system used did not permit sensitive analysis of the hydrogen formed and so the concentration of this gas was determined from mass balance calculations.

The formic acid conversions reported here are given as the ratio of the sum of the CO and CO_2 concentrations in the products to the initial concentration of formic acid introduced while the CO_2 selectivity is given as the ratio of the CO_2 concentration to the sum of the CO and CO_2 concentrations. In the absence of an olefin (i.e. for reactions (1) and (2)), the selectivity to CO_2 also corresponded to the hydrogen selectivity. The hydrogen yield in the experiments without olefins was determined by multiplication of the conversion by the selectivity. In experiments involving one of the olefins, the olefin conversion was determined from the ratio of the concentration of the corresponding alkane formed to the initial concentration of the olefin.

3. Results and discussion

Fig. 1 shows the results of experiments in which the decomposition of formic acid (2.4% in He) was measured as a function of temperature in the presence of ethylene (1 vol.%) and in the absence of ethylene. Fig. 1(a) shows the conversions of formic acid with and without added ethylene and, in the experiment with the olefin present, the corresponding conversions of ethylene; Fig. 1(b) shows the corresponding selectivities to CO_2. Formic acid reacted at temperatures above about 350 K and the conversion was complete at temperatures above 430 K. The catalyst was therefore more active for formic acid decomposition than were any of the palladium-containing alloys studied previously [4], these only giving 100% conversion at temperatures above about 500 K. What is particularly remarkable, however, was that the formic acid conversion in the presence of ethylene was higher than the corresponding conversion without ethylene at all temperatures. The conversion

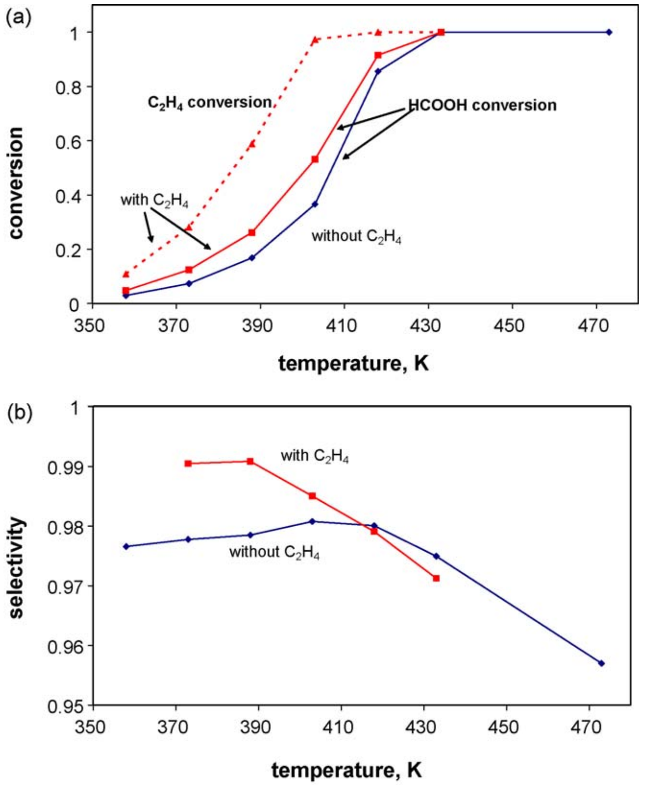

Fig. 1. Steady-state conversions (a) and CO_2 selectivities (b) as a function of temperature for the decomposition of HCOOH and hydrogenation of C_2H_4 by HCOOH over the 10 wt.% Pd/C catalyst (6.8 mg). Gaseous compositions: 2.4 vol.% HCOOH/He and 2.4 vol.% HCOOH/1 vol.% C_2H_4/He, respectively.

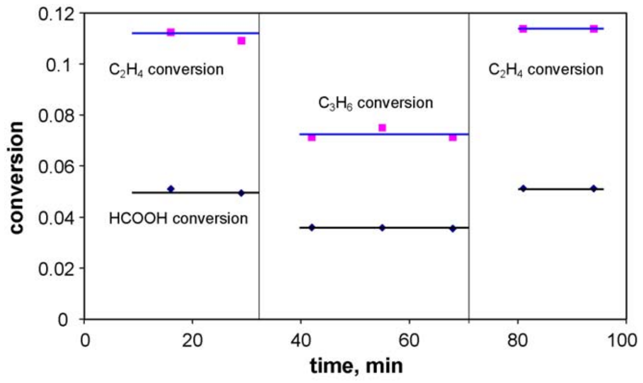

Fig. 2. Comparison of the hydrogenation of C_2H_4 and C_3H_6 by HCOOH over the 10 wt.% Pd/C catalyst (6.8 mg) at 358 K. Gaseous composition: 2.4 vol.% HCOOH/1 vol.% C_nH_{2n}/He.

of formic acid remained constant with time of operation over several hours.

The selectivity to CO_2 was also affected by the presence of ethylene: in the absence of ethylene, the selectivity was about 98% at lower temperatures, dropping to below 96% at 473 K (Fig. 1(b)). When ethylene was present, the selectivity to CO_2 at low temperatures was about 99%, dropping with increasing temperature to a value quite similar to that without ethylene only once the ethylene conversion was almost complete. The water-gas shift (Eq. (3)) and reverse water-gas shift reactions were also examined and it was found that they occurred with significant rates only at higher temperatures (>503 K). Thus, we conclude that neither reaction influences the product distributions during the formic acid reactions over the Pd/C catalyst and that the formation of CO and H_2O takes place in parallel to the formation of CO_2 and H_2, not by the reverse water-gas shift reaction. It has been suggested earlier that formaldehyde is involved as an intermediate in CO formation from formic acid [20]; however, we did not observe any gaseous formaldehyde and so we conclude that only surface formaldehyde species might be involved.

Hydrogen balance calculations carried out at low conversions (i.e. at low temperatures) for the experiments including ethylene (Fig. 1) demonstrated that 95% of the hydrogen produced from the formic acid was consumed for ethane formation (Eq. (4)) and 2% was involved in water formation (Eq. (2)); hence, only 3% was formed as molecular hydrogen (Eq. (1)). In other words, the stoichiometry of the reaction in the presence of ethylene was very close to that of Eq. (4).

Fig. 2 shows the results of an experiment in which the ethylene in the reaction mixture was substituted by propylene. It was found that the propylene could also be hydrogenated effectively by formic acid without any apparent deactivation of the catalyst with time on stream. Separate experiments, not illustrated, showed that as with ethylene, the conversion of the formic acid was higher in the presence of propylene than without it. However, the conversions of propylene and of formic acid were lower than when ethylene was the reactant. Further, re-introduction of ethylene in place of the propylene restored the original conversions. These experiments indicated that the nature of a hydrogen acceptor molecule could also affect the catalytic activity in catalytic transfer hydrogenation reactions.

The hydrogenation of olefins by molecular hydrogen over noble metals is normally considered to take place by reaction of an adsorbed π-complex of the olefin with adsorbed atomic hydrogen [21,22]. It is likely that formic acid adsorbs dissociatively to give a formate species and an adsorbed hydrogen atom; the formate species then dissociate to give gaseous CO_2 and another adsorbed hydrogen atom and the adsorbed hydrogen atoms are then consumed by the adsorbed olefin. That the hydrogenation step is probably fast was indicated by the observation that both the olefins studied could be completely hydrogenated by molecular hydrogen over the Pd/C catalyst used for this work at 313 K, some 100 K below the temperature required for the complete hydrogenation of the olefins using formic acid. Hence, we conclude that the rate of hydrogenation by formic acid is determined by the rate of formation of adsorbed hydrogen from the acid. The results presented here are in line with the recent finding that formic acid provides hydrogen atoms for transfer hydrogenation of double bonds in the liquid phase over a Pd/C catalyst [23].

The apparent activation energies for the CO_2 formation from formic acid without and with added ethylene were determined from the data at low conversions (Fig. 3). Very similar values, 67 and 63 kJ mol^{-1}, respectively, were obtained for the two experiments. This result is consistent with the suggestion that same rate-determining step is involved in both processes; it is hydrogen formation from formic acid. In agreement with this suggestion, the activation energy of ethane formation was also similar (65 kJ mol^{-1}).

The observed difference in conversion observed for ethylene and propylene (Fig. 2) could be explained by the formation of more stable carbonaceous surface species from propylene than from ethylene. These species are not reaction intermediates, but rather spectators [21,24]. They may block the active Pd surface sites for the formation of adsorbed hydrogen atoms from formic acid decomposition, hence decreasing the conversion.

The results of Fig. 1(a) and Fig. 3 show that the conversions of formic acid and the CO_2 formation rates at any temperature over the Pd/C catalyst were slightly higher in the presence of ethylene than those without it. This is probably due to a much lower concentration of gaseous hydrogen in the experiments with olefins, this resulting in a lower occupancy of surface sites by

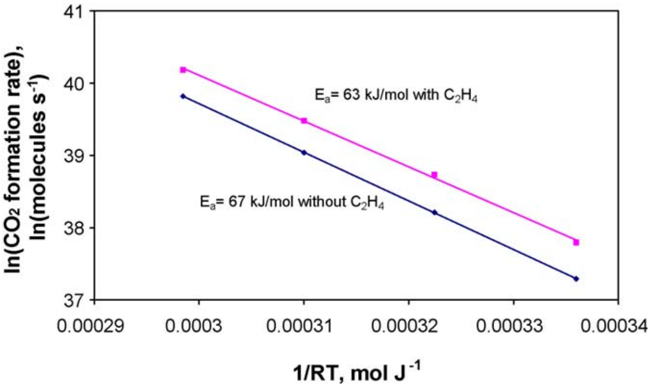

Fig. 3. Arrhenius plots for the conversion of HCOOH to CO_2 in experiments with and without C_2H_4 over the 10 wt.% Pd/C catalyst (6.8 mg) Gaseous compositions as in Fig. 1.

hydrogen. These sites are then available for additional adsorption and reaction of formic acid. In other words, adsorbed hydrogen may block the surface sites for the hydrogen formation from formic acid (Eq. (1)). To explore this possibility, the experiment shown in Fig. 4 was carried out. After 30 min reaction, the He used as diluent gas was substituted by H_2/He mixtures containing 9.8 or 2 vol.% of hydrogen. The increase in hydrogen concentration caused a noticeable decrease in the conversion of the formic acid. The CO_2 selectivity also decreased (Fig. 4(b)). This took place because of the decrease in the CO_2 yield, while the CO yield did not change. When the hydrogen/helium mixture was then replaced once more by helium, the original conversion and selectivity were restored. A similar effect of helium substitution by hydrogen on the rate of formic acid decomposition has been reported by Solymosi and Erdohelyi for supported Rh catalysts [25].

When formic acid is formed in the Biofine Process or in other biomass conversion processes, it will co-exist with significant amounts of water. Hence, if formic acid from biorefinery sources is to be used in hydrogenation reactions, it is important that these reactions are not significantly hindered by the presence of water vapour. Fig. 5 shows the results of an experiment (conversion and selectivity to CO_2) in which the effects of various combinations of reactants were examined. The addition of a low concentration of water vapour had a small positive effect on both the decomposition of formic acid and the hydrogenation of C_2H_4 by formic acid (Fig. 5(a)). There was also a small but noticeable increase in the CO_2 selectivity as a result of water vapour introduction (Fig. 5(b)). Water vapour may slowly interact with adsorbed CO providing bigger concentration of active sites for formic acid decomposition.

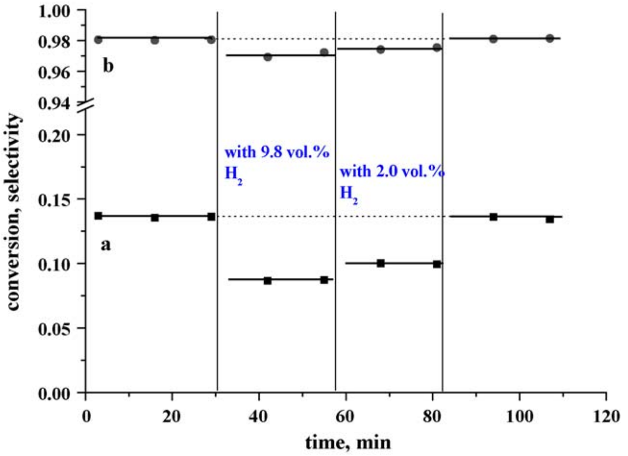

Fig. 4. The effect of hydrogen on (a) the conversion of HCOOH and on (b) the selectivity to CO_2. Catalyst 6.8 mg of 10 wt.% Pd/C; temperature 383 K; gaseous composition 2.4 vol.% HCOOH, balance He or H_2/He.

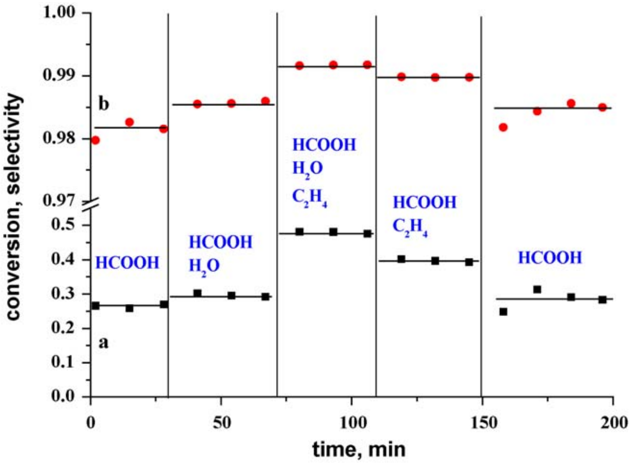

Fig. 5. The effects of water vapour and C_2H_4 on (a) the conversion of HCOOH and (b) the selectivity to CO_2 for the decomposition of HCOOH over the 10 wt.% Pd/C. Reaction temperature: 398 K; gaseous compositions: 2.4 vol.% HCOOH, 2.4 vol.% HCOOH/2.3 vol.% H_2O, 2.4 vol.% HCOOH/2.3 vol.% H_2O/1 vol.% C_2H_4, 2.4 vol.% HCOOH/1 vol.% C_2H_4; balance He in all cases.

It was of interest to know if gold-containing catalysts could also be used for formic acid decomposition and transfer hydrogenation. Fig. 6 shows the results for the decomposition of formic acid to hydrogen using two different materials, 1 wt.% Au/TiO_2 and 0.8 wt.% Au/C, and also shows for comparison the results for the Pd/C catalyst. Both gold samples had some activity for hydrogen production but were significantly less active than the Pd/C sample. The titania-supported material was more active than the carbon-supported one. Note that the mean particle diameter in the carbon-supported catalyst was three times bigger than that in the titania-supported one [18]. It has been shown earlier that smaller gold particles supported on titania [26,27] as well as on activated carbon [28] are more active in, for example, CO oxidation. The existence of a synergetic effect between the small gold particles and the titania support may not also be excluded [26,27].

In contrast to the Pd/C and Au/C samples, which gave predominantly CO_2 and H_2 (Eq. (1)), the Au/TiO_2 sample gave significant quantities of CO and water (Eq. (2)). Also, in contrast to the results for the Pd/C sample, when ethylene or propylene was added to a formic acid feed passing over the gold catalysts, no hydrogenation was observed over the gold catalysts.

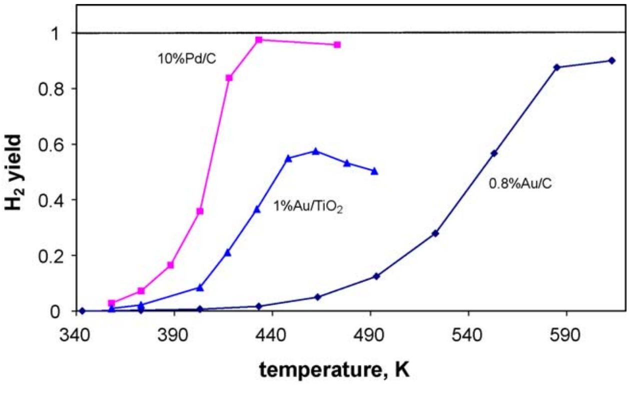

Fig. 6. Comparison of hydrogen yields as a function of temperature for the decomposition of HCOOH over the 10 wt.% Pd/C, 1 wt.% Au/TiO_2 and 0.8 wt.% Au/C catalysts taken with the following weights 6.8, 69 and 85 mg, respectively. Gaseous composition: 2.4 vol.% HCOOH/He.

It has been reported in the literature that gold catalysts have some activity in some hydrogen transfer reactions [17]. Gold catalysts may also give the hydrogenation of acetylene [27,29], propyne [30] and some alkadienes and ketones [27] using molecular hydrogen. However, in contrast to other noble metals such as Pt and Pd, they do not hydrogenate ethylene and propylene to any significant extent [29,30]. Gold nanoparticles may also adsorb large amounts of acetylene, but they do not adsorb ethylene or propylene [29,31]. Adsorbed hydrogen is also necessary to give hydrogenation, but the extent of hydrogen adsorption has been shown to be quite limited on gold [29,32] because the interaction of hydrogen with gold is weaker than that with Pt [32]. Hence, gold catalysts do not provide sufficiently high concentrations of the reactive intermediates needed for ethylene and propylene hydrogenation by formic acid, a result which is in accordance with the results of the earlier papers [29,31]. This is also consistent with the proposed mechanism involving the formation of surface hydrogen from formic acid followed by hydrogenation of the adsorbed olefins by this adsorbed hydrogen.

4. Conclusions

It has been shown that olefins like ethylene and propylene can be hydrogenated effectively in the vapour phase over a Pd/C catalyst by using formic acid instead of hydrogen. The use of formic acid in hydrogenation reactions would avoid the need for the separate steps involved in hydrogen production (e.g. from natural gas) as well as its storage, transportation and supply. Using formic acid instead of hydrogen could also be useful for some other reactions, for example in the hydrogenation [12,14,15] or reduction/hydrodeoxygenation [16] of biomass-derived intermediates necessary for the production of fuel additives.

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