



Formic acid decomposition over palladium based catalysts doped by potassium carbonate



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This paper is dedicated to the memory of Alfred Ross (1901–1948, father of Julian Ross) Who carried out some of the earliest work on infrared spectroscopy (A. Ross, "Absorption Spectra of Pyrone Derivatives in the Near Infra-Red", Proc. Royal Soc. A, 113 (1926) 208–220) and who inspired Julian's interest in spectroscopic methods.

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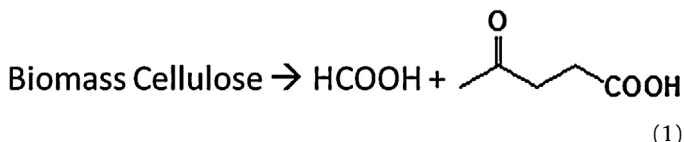
ABSTRACT

The introduction of potassium carbonate into Pd/Al₂O₃, Pd/SiO₂ and Pd/C catalysts promoted both the catalytic activities and the hydrogen selectivities for the vapor-phase formic acid decomposition, giving values of the turnover frequency (TOF) at 343 K that were 8–33 times higher than those for the undoped samples. The apparent activation energies over all the K-doped samples increased considerably, this showing that there is a difference in the reaction path between the doped and the undoped catalysts. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) has been used to gain an understanding of the nature of the species formed in the Pd/SiO₂ catalysts during the reaction. This study showed that a considerable fraction of the HCOOH was condensed in the pores of the catalysts and that the introduction of potassium contributed to the formation of buffer-like solution. The existence of mobile formate ions present in the buffer solution and stabilized by K ions in a K-doped catalyst is an essential factor in the promotion of its activity.

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1. Introduction

Formic acid is a relatively low-volume chemical and it has limited uses; these include its application as a preservative and antifungal agent as well as in the production of leather and as a lime scale remover. It may be produced by chemical methods such as the hydrolysis of methyl formate but it is also produced in equimolar proportions, together with levulinic acid, by the hydrolysis of biomass-derived cellulosic raw materials [1]:



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With the current increase in interest in the production of levulinic acid and other valuable chemicals from biomass, it becomes important to develop ways of using the by-product formic acid as this is otherwise a waste material. For many years, the decomposition of formic acid according to Eqs. (2) and (3):



was used as a test reaction to distinguish between catalysts with dehydrogenation (Eq. 2) and dehydration (Eq. 3) properties [2,3]. More recently, however, there has been considerable interest in the use of the decomposition reaction as a means of producing pure hydrogen for use, for example, in fuel cell applications; in this work, the main aims are to produce predominantly hydrogen and CO₂, with minimal CO contents, at as low temperature as possible [4–9]. In our initial work, we showed that a commercial Pd/C catalyst gave 100% conversion of formic acid vapor at a temperature of 433 K with

selectivity to hydrogen and CO₂ of 95–99% [10]. We also showed that it was possible to use the same catalyst to hydrogenate an olefin with formic acid stoichiometrically at the same temperature [11].

More recently, we have been probably first to demonstrate that the rate of formic acid vapor conversion over a Pd/C catalysts could be increased very significantly by the introduction of alkali metal ions into the catalyst and that the hydrogen and CO₂ selectivities were also increased very significantly by the alkali promotion [6,12]. We presented evidence showing that the promotional effect in K-promoted Pd/C catalysts is due to the presence in the pores of the support of a buffer solution consisting largely of potassium formate and formic acid [6]. We suggested that the rate-determining step in the decomposition reaction is the decomposition of formate anions at the surface of the Pd crystallites; as soon as a formate anion decomposes, it is replaced by the dissociation of a formic acid molecule, the concentration of the latter being replenished constantly from the gas phase. Evidence for this mechanism was obtained by careful observation of changes in the gas phase composition occurring during the early stages of the reaction prior to the establishment of steady-state behavior. Despite attempts to observe the reacting species using infrared techniques, we were unable to do this because of the lack of transparency to IR radiation of the carbon support.

The aim of the work presented in this paper was initially to examine whether or not palladium supported on an infrared-transparent material such as silica or alumina is an effective catalyst for the decomposition of formic acid and whether or not such materials can then be promoted by the addition of K⁺ ions. Then, having shown that the Pd/SiO₂ catalyst gave significant rates of formic acid decomposition with good selectivity to hydrogen and that K⁺ also gave significant promotion with this material, further experiments using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) were carried out and the results, which support the mechanism previously postulated, are also presented. The value of the use of in-situ infrared spectroscopy has previously been demonstrated for formic acid interaction with supported metals [9,13,14].

2. Experimental

The unpromoted catalysts used in this work were supplied by Johnson Matthey (1.0 wt.% Pd/SiO₂, 1.0 wt.% Pd/Al₂O₃) and Sigma-Aldrich (1.0 wt.% Pd/C). The incipient wetness impregnation method was used to deposit potassium carbonate on each of these Pd-containing samples [6,12]. The measurements of catalytic activities for formic acid decomposition in the vapor phase were carried out in a fixed-bed flow reactor. The weight of the catalysts was chosen to give 0.68 mg of Pd for each set of experiments. All the samples were reduced in 1 vol.% H₂/Ar at 573 K for 1 h and cooled in He to the reaction temperature prior to testing. A mixture of 2 vol.% formic acid in He at a total flow rate of 51 cm³ (STP) min⁻¹ was then introduced into the reactor system using a syringe pump (Sage). The reactants and products were analyzed by a gas chromatograph (HP-5890) fitted with a Porapak-Q column and a TCD detector. The details of the activity tests carried out were given in Refs. [7,10].

A SpectraTech-0030 DRIFTS “in situ” cell was used for the infrared measurements, this being fitted with ZnSe windows. The cell was mounted in a Nicolet Magna 560 FT-IR spectrometer with an MCT detector; it was attached to the same gas-flow system used for the catalytic measurements and the same pretreatments, flow rates and gas compositions were used. A sample of the catalyst (Pd/SiO₂, 12.7 mg or K-Pd/SiO₂, 16.8 mg) to be examined was introduced into the sample holder of the cell and it was reduced in a flow of 1 vol.% H₂ in Ar at 573 K for 1 h. The sample was then cooled

in the He flow and single beam scanning was carried out at several temperatures to provide background spectra for the subsequent in-situ catalytic measurements at the corresponding temperatures. A 2 vol.% formic acid/He mixture was then introduced into each catalyst sample at 333 K and absorbance spectra were recorded as a function of time until stable spectra were obtained (30 min). Finally, the formic acid containing feed gas was replaced by pure He and the temperature was then increased. The corresponding absorbance spectrum at each temperature was recorded until it did not change with time.

The Brunauer–Emmet–Teller (BET) surface areas of all the samples after pretreatment in a flow of nitrogen at 473 K for 2 h were measured by nitrogen adsorption using a Micromeritics Gemini system. Transmission electron microscopy (TEM) images were obtained for the reduced catalysts with a JEOL JEM-2100F (200 kV) microscope.

3. Results

3.1. Characterization of catalysts

Table 1 shows the BET surface areas and particle sizes of the catalysts studied. The BET surface area of the Pd/C sample was 933 m² g⁻¹, a factor of 2.5 times higher than that of the Pd/SiO₂ sample and 5 times higher than that of the Pd/Al₂O₃ sample. We showed in our previous work [6,12] using a C support that a very high potassium content corresponding to a weight ratio of 10:1 of K: Pd gave the most active catalyst with even distribution of K ions through the sample. On the basis of the BET surface areas of the Pd/SiO₂ and Pd/Al₂O₃ samples, we therefore chose to prepare samples with weight ratio values of 4:1 for the K–Pd/SiO₂ and 2:1 for K–Pd/Al₂O₃ to ensure that the potassium ions were also evenly dispersed over the whole surface of these samples; no further attempts were made to optimize the K/Pd ratios. The average Pd particle size obtained from TEM images for the silica-supported catalyst is around 7.4 nm, which is larger than those found for the samples supported on alumina (4.2 nm) and activated carbon (3.6 nm) shown in Table 1.

3.2. Catalytic activity data

Fig. 1(a) shows the results of activity tests for formic acid decomposition over the carbon-, silica- and alumina-supported Pd catalysts as well as the corresponding data for the K-promoted samples while Fig. 1(b) shows the values of the corresponding selectivities to hydrogen. The catalytic behavior of the Pd/SiO₂ sample was close to that of the Pd/C sample, the conversions for the former sample being only slightly lower than those for the latter at all temperatures; the reaction temperatures required to give 50% conversion of the formic acid over Pd/SiO₂ and Pd/C were both around 385 K. The Pd/Al₂O₃ sample was significantly less active than the other two samples; the temperature for 50% conversion was approximately 30 K higher. The differences in selectivities were even more marked: the hydrogen selectivity remained above 92%

Table 1
Characteristics and kinetic data for the catalysts studied.

Catalysts	BET surface area (m ² g ⁻¹)	Mean particle size (nm)	TOF at 343 K (s ⁻¹)	Activation energy (kJ mol ⁻¹)
1 wt.% Pd/C	933	3.6 ± 1.7	0.008	65
10:1 K–Pd/C	688	3.7 ± 1.3	0.27	97
1 wt.% Pd/SiO ₂	380	7.4 ± 2.4	0.0095	78
4:1 K–Pd/SiO ₂	–	–	0.079	95
1 wt.% Pd/Al ₂ O ₃	144	4.2 ± 1.0	0.010	49
2:1 K–Pd/Al ₂ O ₃	–	–	0.075	84

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