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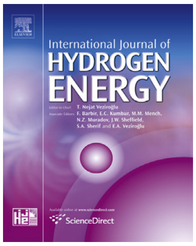

Pd/C nanocatalyst with high turnover frequency for hydrogen generation from the formic acid–formate mixtures

Xin Wang [a], Gong-Wei Qi [a], Chun-Hui Tan [a], Ye-Ping Li [a], Jing Guo [a], Xin-Jing Pang [a], Shu-Yong Zhang [a,b,*]

[a] School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, PR China
[b] State Key Laboratory of Crystal Material, Shandong University, Jinan 250100, PR China

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ABSTRACT

Pd/C nanocatalyst with high turnover frequency (TOF) for hydrogen generation from the formic acid (FA)–sodium formate (SF) mixtures was prepared via an ex situ reduction of $PdCl_2$ used formate in the presence of citric acid. The morphology and property of the Pd/C catalyst before and after decomposition of FA–SF mixture were characterised using transmission electron microscopy, high-resolution transmission electron microscopy, X-ray photoelectron spectroscopy, energy dispersive spectroscopy, X-ray diffractometer and Fourier transform infrared spectrometer. Over this Pd/C catalyst, a TOF of 228.3 h^{-1} was observed for a FA–SF mixture with a FA/SF ratio of 1:9. The observed TOF was the highest ever reported for heterogeneous Pd/C catalysts. The deactivation of the Pd/C catalyst was attributed to desorption of citric acid, reduction of Pd^{II} content and adsorption of CO. Washing and drying could partially recover the activity of the Pd/C catalyst.

1. Introduction

Hydrogen has long been considered the most promising energy source in the future [1]. However, advances in the application of hydrogen are greatly limited because of its high-energy requirements during preparation and the hazards of its storage and transport [2,3]. Thus, suitable media for hydrogen storage and efficient approaches for controllable hydrogen generation have become the focus of research over the past decade. Although methanol, ethanol and sodium borohydride are studied with great interest [4–6], formic acid (FA) and sodium formate (SF) are gaining increased attention as hydrogen storage media [7–13]. FA, SF, or their mixtures can be catalytically decomposed by either homogeneous or heterogeneous catalysts. The facile control of hydrogen generation makes heterogeneous catalysts attractive [14–16]. Some binary catalysts and single-component catalysts with well-defined structures improve catalytic activity [7,15], but Pd-based nanocatalysts are of particular interest because of their high catalytic activity and facile preparation. FA, SF and their mixtures were successfully decomposed on Pd/C catalysts at 60 °C in the late 1970s and 1980s [17–19]. Recently, an integrated in situ method to prepare Pd/C catalysts with a

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[*] *Corresponding author*. School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, PR China. Tel.: +86 531 88361378; fax: +86 531 88364781.

E-mail address: syzhang@sdu.edu.cn (S.-Y. Zhang).

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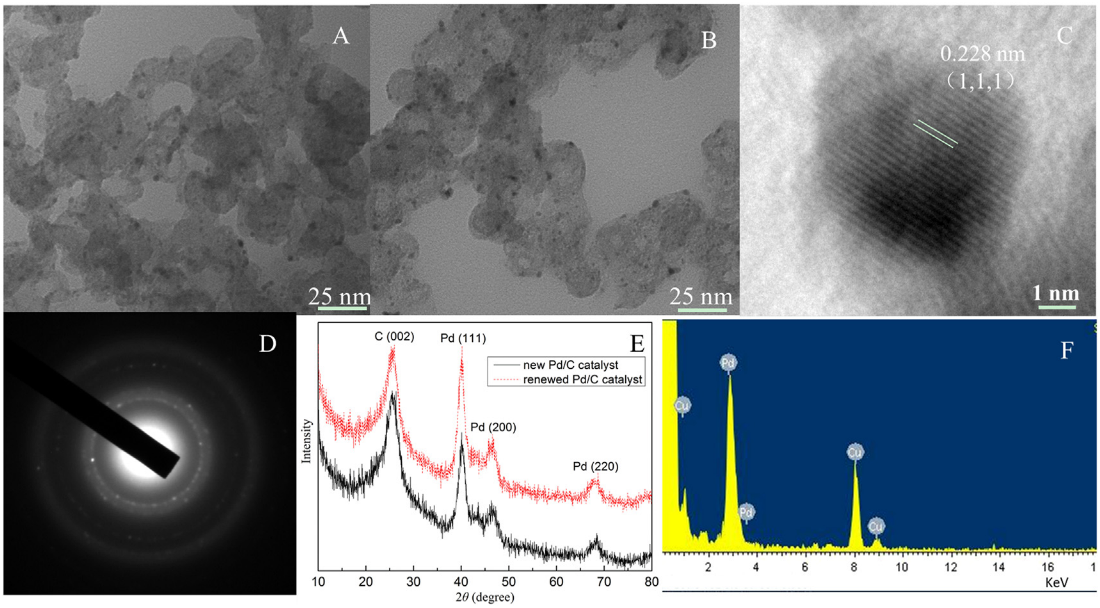

Fig. 1 – Characterisation of the newly prepared Pd/C catalyst. (A) TEM, (C) HRTEM, (D) electron diffraction, (E) XRD, and (F) EDX. (B) is the TEM of the renewed Pd/C catalyst.

relatively high turnover frequency (TOF) of 64 h^{-1} was reported [20], but this value was still lower compared with that of most homogeneous catalysts.

This study synthesised a heterogeneous Pd/C catalyst by an ex situ reduction strategy similar to that reported in reference [20]. The catalysed decomposition of FA, SF and FA–SF mixtures on as-prepared catalysts was tested.

2. Experimental

2.1. *Material*

$PdCl_2$ was purchased from Runjie Chemical Corp. (Shanghai, China). FA and SF were of analytical grade. Ultrapure water (Millipore, 18.25 MΩ cm) was used throughout the solution preparation.

2.2. *Catalyst preparation*

Vulcan XC-72 activated carbon (1 g) was dispersed in 60 mL of 10 wt.% NaOH with the aid of an ultrasonic stirrer for 30 min and heated at 90 °C for 1.5 h. The mixture was rinsed with deionised water to pH 7, boiled at 120 °C in a 1:1 (V/V) HNO_3:H_2SO_4 mixture for 2 h, washed to neutral and dried in an electric oven at 60 °C for 10 h.

The pre-treated Vulcan XC-72 carbon (190 mg) was ultrasonically dispersed in 3.6 mL of 0.0262 mol dm^{-3} $PdCl_2$ for 1 h. The dispersion was adjusted to pH 7 with 0.1 mol dm^{-3} Na_2CO_3 solution. Then, 10 mL solution containing 2 g SF and 0.06 g citric acid was added dropwise into the mixture under strong magnetic stirring for 30 min. The Pd/C catalyst was filtered and washed with deionised water until no Cl^- was detected. The Pd/C catalyst was then dried in a vacuum oven at 60 °C for 2 h and stored in a desiccator for further use.

2.3. *Catalyst characterisation*

JEM-2100 high-resolution transmission electron microscopy (HRTEM, JEOL, Japan), JEM-1011 transmission electron microscopy (TEM, JEOL, Japan) and INCA Sight X Energy dispersive spectroscopy (EDX, Oxford, USA) were used to characterise the composition and morphology of the as-prepared Pd/C catalyst. Crystographic information was collected by a D8 Advance X-ray diffractometer (XRD, Bruker, Germany). VERTEX-70 Fourier transform infrared spectrometer (FTIR, Bruker, Germany) was used to record the FTIR spectra. The XPS spectra were measured by ESCALAB-250 X-ray photoelectron spectroscopy (XPS, Thermo fisher scientific, UK).

2.4. *Testing of catalyst*

The effect of FA/SF ratio on the activity of the Pd/C catalyst was investigated in 30 mL solution with different FA/SF ratios, namely, 1:0 (pure FA solution), 4:1, 1:1, 1:4, 1:5, 1:9 and 0:1 (pure SF solution). The total concentration of FA and SF in these solutions was 2 mol dm^{-3}.

The solutions with different FA/SF ratios were decomposed in a flask with 20 mg Pd/C catalyst (9.43×10^{-6} mol Pd). Hydrogen volume was measured during the 2 h reaction after the CO_2 and CO by-products were removed by NaOH and CuCl solutions respectively. CO_2 removal was confirmed by limewater. Hydrogen generation was measured using a gas burette. TOF was calculated according to the following equation:

$$\mathrm{TOF} = \frac{pV_{H_2}}{RTn_{Pd/C}t} \qquad (1)$$

where p is the pressure, V_{H_2} is the released hydrogen volume, R is the gas constant, T is the temperature, $n_{Pd/C}$ is the mole of Pd/C catalyst and t is the reaction time in hour.