Low Activation Energy Dehydrogenation of Aqueous Formic Acid on Platinum-Ruthenium-Bismuth Oxide at Near-Ambient Temperature and Pressure

Siu-Wa Ting, Shaoan Cheng, Kwok-Ying Tsang, Nicole van der Laak, and Kwong-Yu Chan[*]

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, P.R. China

[*]E-mail: hrsccky@hku.hk; Fax: +852 28571586

1. Experimental

Synthesis:

The catalysts were prepared by the citric acid gel method[s1,s2] using metal precursors of $RuCl_3.xH_2O$, $H_4PtCl_6.H_2O$ (Fluorochem), and $Bi(NO_3)_3.5H_2O$ (Merck) dissolved in water and with citric acid (Alfa Aesar) added as a protecting agent. Vulcan carbon 72 XC was added to adsorb the metal precursors. The mixture was heated in an oil bath at 100 °C until all the water was evaporated. Subsequently, the powder was heated at 850°C in inert atmosphere to obtain the final product catalyst.The heating rate employed was 2℃ /min and kept at 850°C for 4 hours.

Activity test:

Decomposition of formic acid experiment was performed with premixed formic acid solution heated to the desired temperature and added to a stoppered Erlenmeyer flask containing the catalyst and immersed in a water bath at constant temperature. The volume of gas liberated at near atmospheric pressure was measured by a gas burette after passing through a water trap. The gas product composition was analyzed by a gas chromatography analyzer (GC) from Perkin Elmer equipped with a thermal conductivity detector (TCD) and a six-port valve for intermittent in-line sampling.

2. <u>Gas analyses</u>

A Perkin Elmer Gas chromatography Analyzer (GC) with a thermal conductivity detector (TCD) for separating and analysing a H_2, CO, CO_2 air mixture was used to analyze the product gas evolved from formic acid decomposition. A standard gas sample conprising of 4.969% CO_2, 4.957% CO, 4.978% N_2, 4.990% O_2, 4.141% H_2, and 4.032% CH_4 was used to calibrate the GC with the chrommatograph shown in Fig. S1(a). The H_2, CO and CO_2 peaks can be well resolved. The product gas was sampled intermittently after adding the formic acid into reactor flask containing the catalyst. Five gas chromatographs were recorded for each sampled gas at a particular time. The carrier gas is helium at 2 psig. A typical product gas chrommatograph is shown in Fig. S1(b) and the analyzed gas composition over a 2 hour period is shown in Table S1.
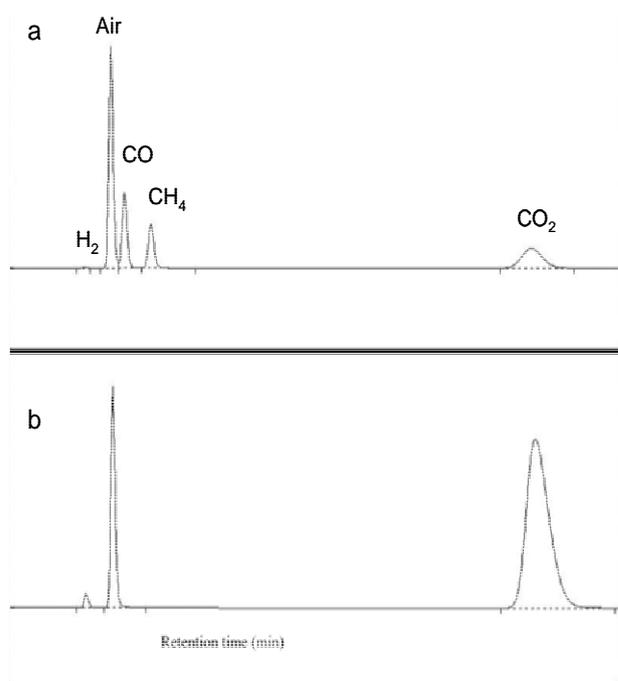

Figure S 1. Gas chromatographs of (a) reference standard (b) the gas evolved from catalytic decomposition of formic acid.

Time (min)	% of H_2	% of CO_2
4-11	0.52$\pm$ 0.04	0.48$\pm$ 0.04
12-36	0.52$\pm$ 0.01	0.48 $\pm$0.01
36-78	0.51$\pm$ 0.01	0.49$\pm$ 0.01
78-120	0.50$\pm$ 0.04	0.50$\pm$ 0.03

Table S1. The product gases composition analyzed by GC

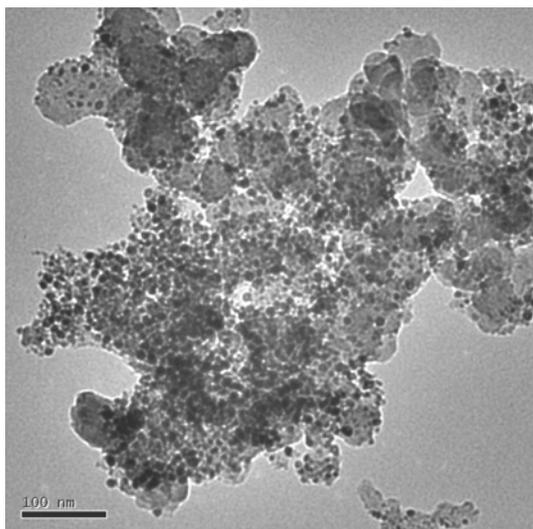3. <u>Examples of typical PtRuBiO$_x$ catalysts and their performance</u>

Figure S 2.   Transmission electron microscopy image of Catalyst with Pt:Ru:Bi ~ 3:1:1
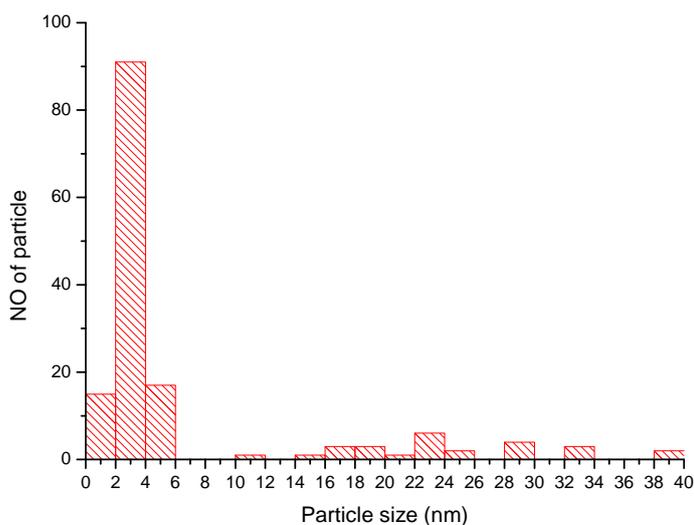
Figure S 3. Particle size distribution of Catalyst used for the reaction shown in Figure 1

The Volume-area mean diameter $\quad d_{VA} = \dfrac{\sum n_i d_i^{\,3}}{\sum n_i d_i^{\,2}}$

The Volume-area mean diameter of this sample was 26.5nm.

Dispersion D= $\dfrac{N_S}{N_T} = \dfrac{6\dfrac{v_m}{a_m}}{d_{VA}}$

Assuming the case of pure Pt, D =4.23% and for the assumption of rure Ru gives D = 4.86%.

D is 4.55% if the catalyst is assumed to be the average of Pt and Ru.

According, the turn over frequency base on surface metal atoms (PtRu) is TOF=312 hr-1 average over the first hour. For the detail of calculation please find the handbook of heterogeneous catalyst [S3]

	Metal mol ratio in precursor			Total Metal Loading wt %	Initial gas generation rate in the first minute of reaction. (ml/min)	Steady state gas generation rate (ml/min)
Sample	Pt	Ru	Bi	-	-	-
1	1	1	0.5	23	15.8	0.31
2	3	1	1	40	60	3.49
3	2	1	1	34	21	0.70
4	1	3	1	34	69.8	5.80
5	1	2	1	31	15	0.12
6	2	1	4	30	26.3	3.10
7	1	0.8	0.1	18	29.5	1.60

Table S2. Compositions of typical $PtRuBiO_x$ prepared and decomposition rates of 80ml 15% v/v formic acid at 80°C with 250mg catalyst.

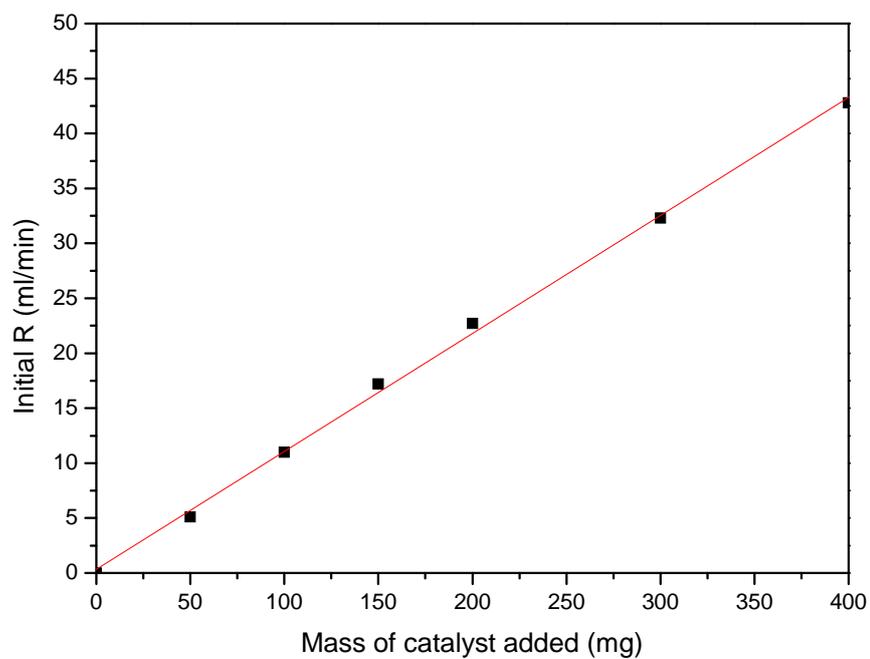4.   Rate dependence on catalyst mass.

Figure S 4 The initial rate of Pt-Ru-BiO$_x$ on Vulcan XC 72 carbon (Pt/Ru/Bi ~ 2:1:4) towards formic acid (80 ml 15% v/v) decomposition at 80°C with different mass of catalysts.

5.   X-ray photoelectron spectroscopy (XPS)

XPS spectra were collected on Physical Electronics 5600 multi-technique system.
The binding energy scale was referenced to the C1s signal of 284.5 eV. Spectra were
fitted after Shirley background correction.

Two peaks with binding energies of 71.49eV and 74.82eV, 72.43eV and 75.76eV,
74.19eV and 77.52eV correspond to Pt $4f_{7/2}$ and Pt $4f_{5/2}$ state of metallic Pt^o , Pt^{II} and Pt^{IV}
respectively [S3]. For bismuth of the XPS spectrum, the doublet can be resolved clearly into
two peaks with binding energies at 158.95eV for Bi $4f_{7/2}$ and 164.26eV for Bi $4f_{5/2}$. These
peaks correspond to a +3 oxidation state of bismuth [S3] . The peaks with binding energies
529.56ev and 530.85ev correspond to O 1s state of metal oxides and hydroxides
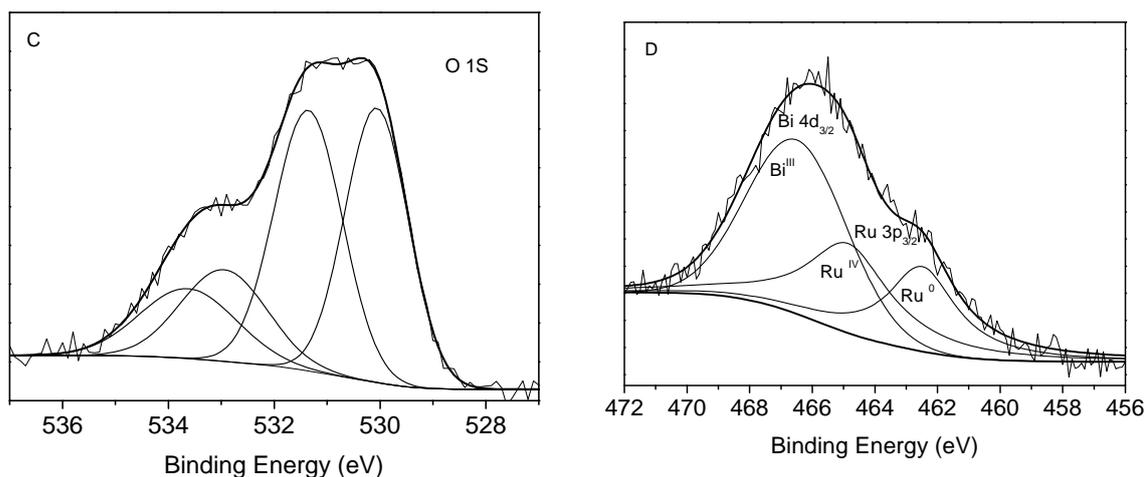respectively [S3]
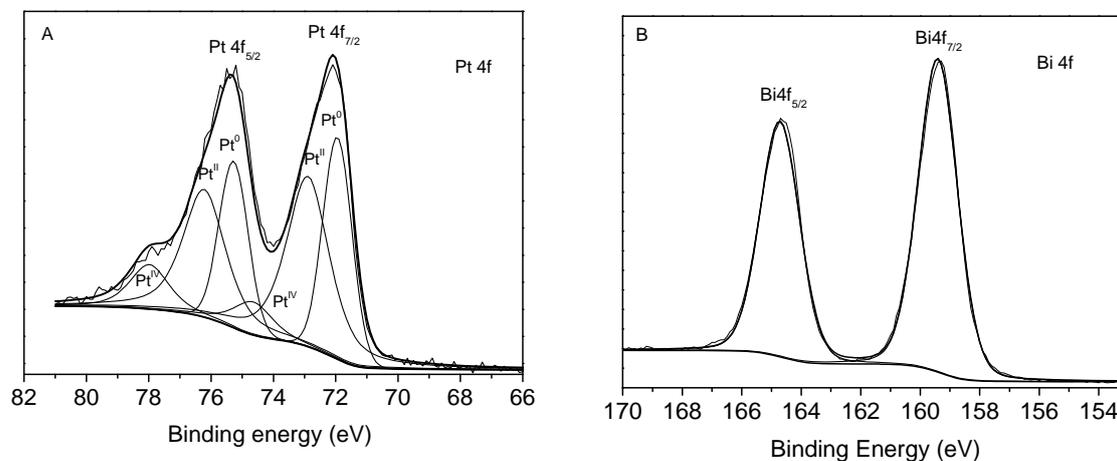
Figure S 5 XPS spectra showing (A) Pt peaks, (B) Bi peaks (C) O peaks and (D) Ru and Bi Peak

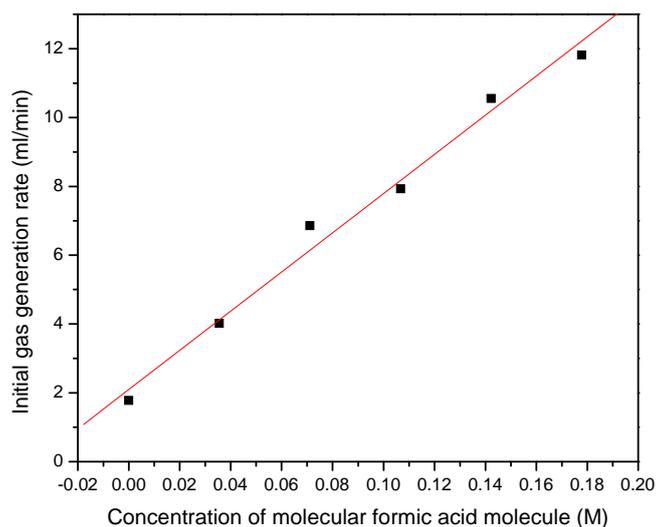6.   Dependence on formate ion and formic acid concentrations

Figure S 6   Rate of decomposition as a function of formic acid concentration. Formate ion is present in excess as sodium formate initially at 2.33M. Molecular formic acid was induced by addition of HCl and the x-axis shows the value calculated via ionic equilibrium with known K_a of formic acid.
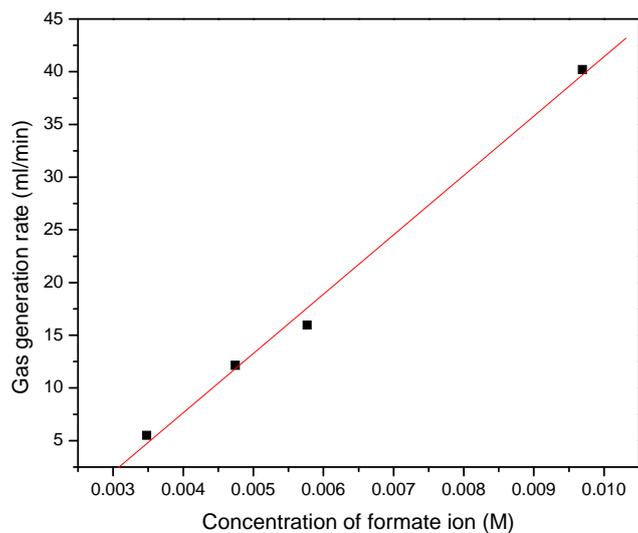
Figure S 7 Rate of decomposition as a function of formate ion concentration. Formic acid is

present in excess initially at 2.33M with some dissociated into formate ion. The formate ion concentration was adjusted negatively by adding HCl to shift equilibrium towards molecular formic acid and the x-axis shows the value calculated via ionic equilibrium with known Ka of formic acid.
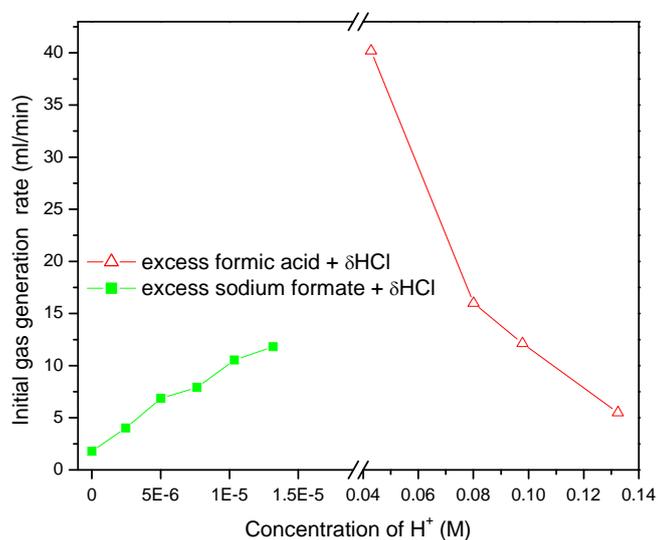

Figure S 8 Rate of decomposition as a function of proton concentration combining the data of experiments of Fig. S6 and Fig. S7   but with calculated proton concentration in the X axis. The results show no consistent dependence of formic acid decomposition on pH.

7. CO chemisorption measurement of a PtRuBiO$_x$ (1:3:1) on Vulcan XC 72 carbon catalyst with 34% total metal loading. The results were compared with the CO chemisorptions on a commercial PtRu on carbon catalyst with 55% metal loading.

The measurements were performed only once with a Micromeritics ASAP 2020 physisorption/chemisorption instrument. The samples were degassed overnight. Analyses were carried out first with pretreatment in hydrogen for 2 hours at 350°C. The CO sorption was carried out at 35 °C.

	PtRuBiO$_x$ on carbon	PtRu on carbon
Metallic Surface Area adsorbed with CO	0.144 m^2/g sample	18.5 m^2/g sample
Metallic Surface Area adsorbed with CO	0.426 m^2/g metal	35.1 m^2/g metal

References

[S1]   J. W. Guo, T. S. Zhao, J. Prabhuram, R. Chen and C. W. Wong, *Electrochim Acta* 2005, **51**, 754.

[S2]   M. Anilkumar, R. Pasricha and V. Ravi, *Ceram Int* 2005, **31**, 889.

[S3]   G. Ertl, H. Knözinger, and J. Weitkamp, *Handbook of heterogeneous catalysis*, VCH, Munich, 1997.

[S4]   J. F. Moulder, W. F. Stickle, P. E. Sobol and K. D. Bomben., *Handbook of X-ray Photoelectron spectroscopy*, Physical Electronics, Inc, Minnesota, 1995.