Supporting information

Organosoluble Zirconium Phosphonate Nanocomposites and their Supported Chiral Ruthenium Catalysts: the first Example of Homogeneization of Inorganic-Supported Catalyst in Asymmetric Hydrogenation

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1. ^{1}H NMR, ^{13}C and ^{31}P NMR of compounds **1a-e** (**Figure S1-S5**)

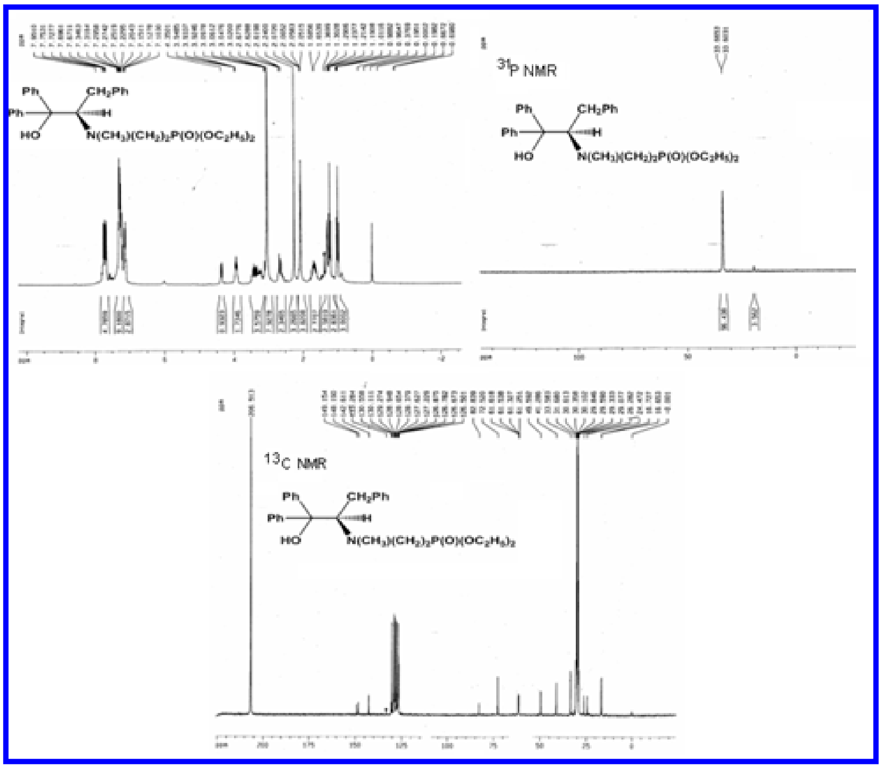


Figure S1. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR of phosphonate **1a**

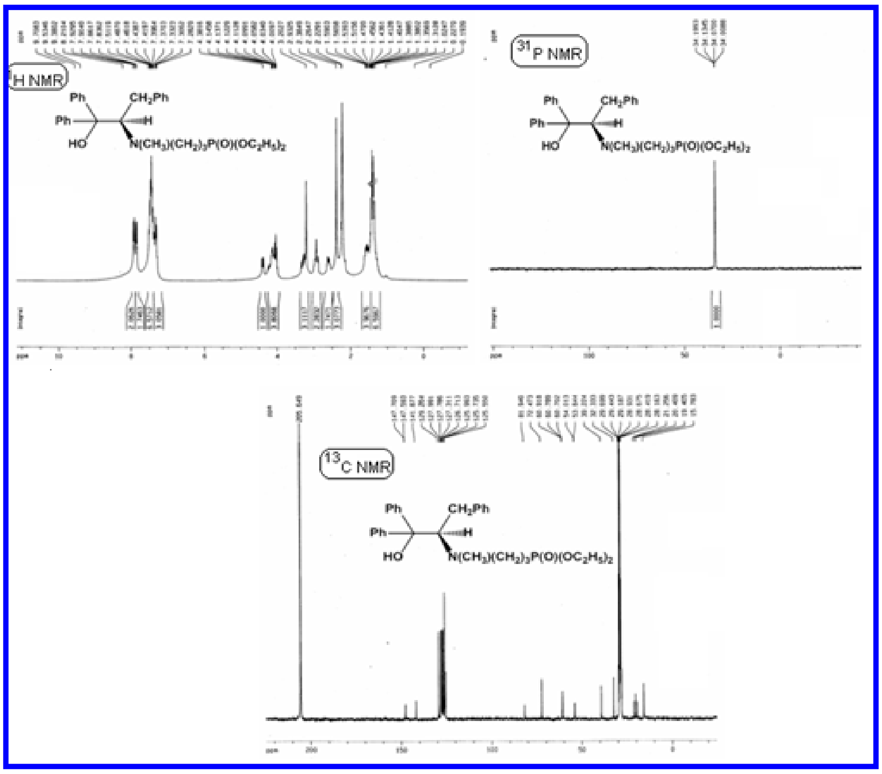


Figure S2. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR of phosphonate **1b**

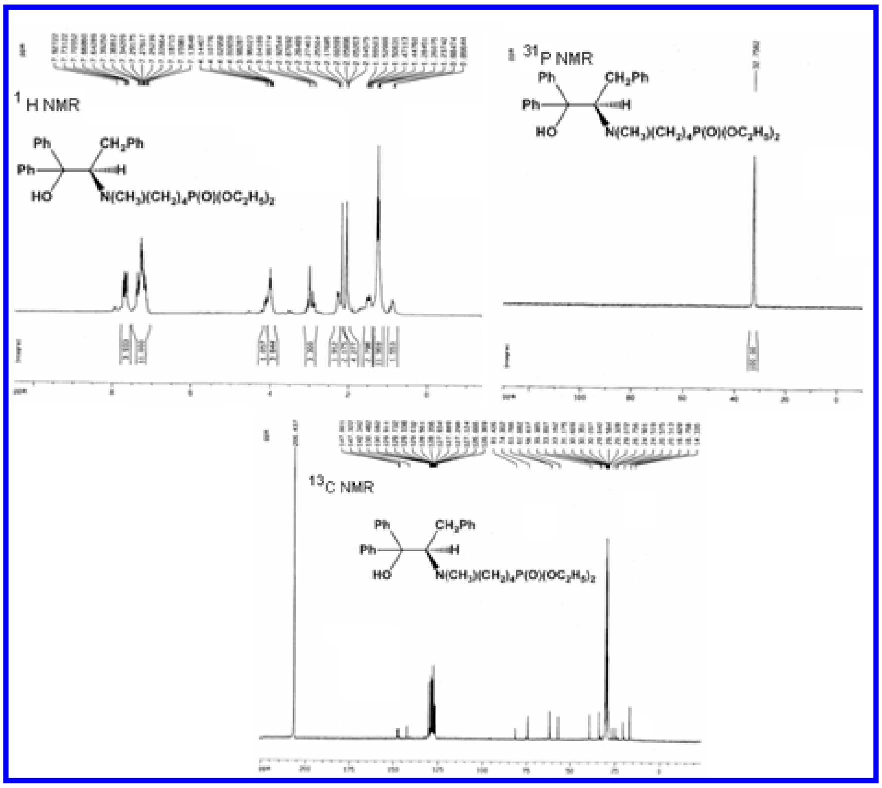


Figure S3. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR of phosphonate **1c**

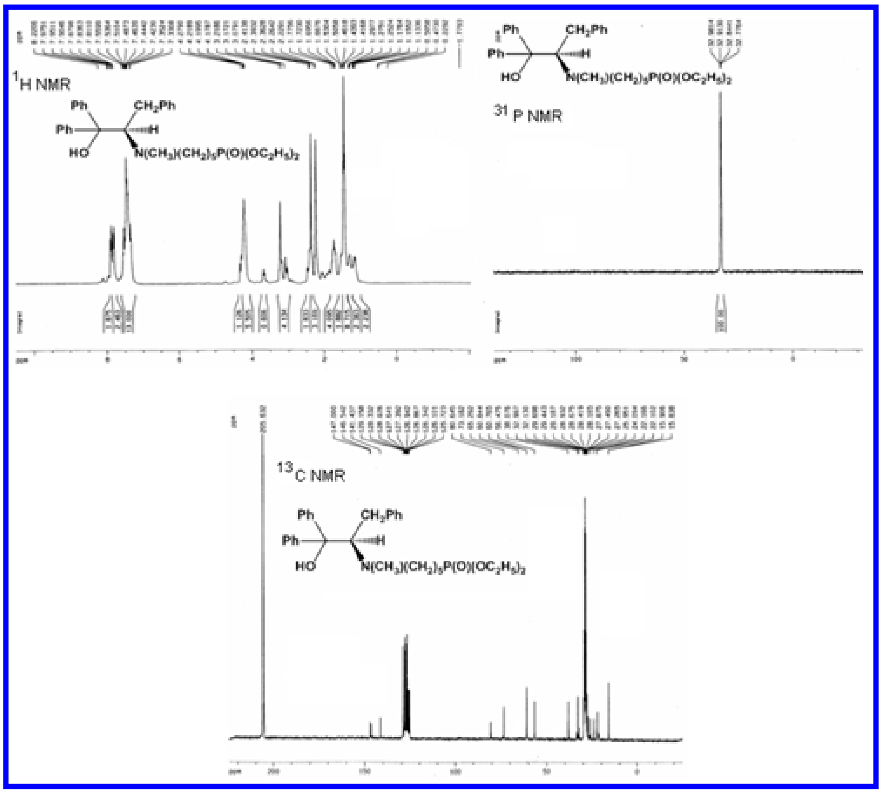


Figure S4. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR of phosphonate **1d**

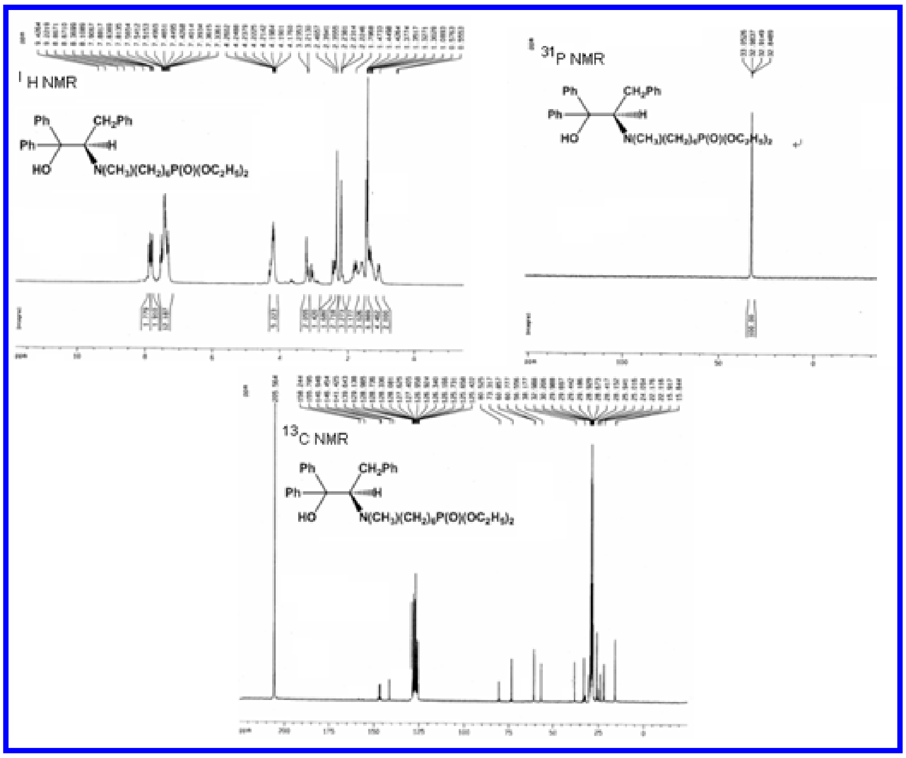


Figure S5. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR of phosphonate **1e**

2. The solid state ^{13}C and ^{31}P NMR of zirconium phosphonate **2b** (**Figure S6**)

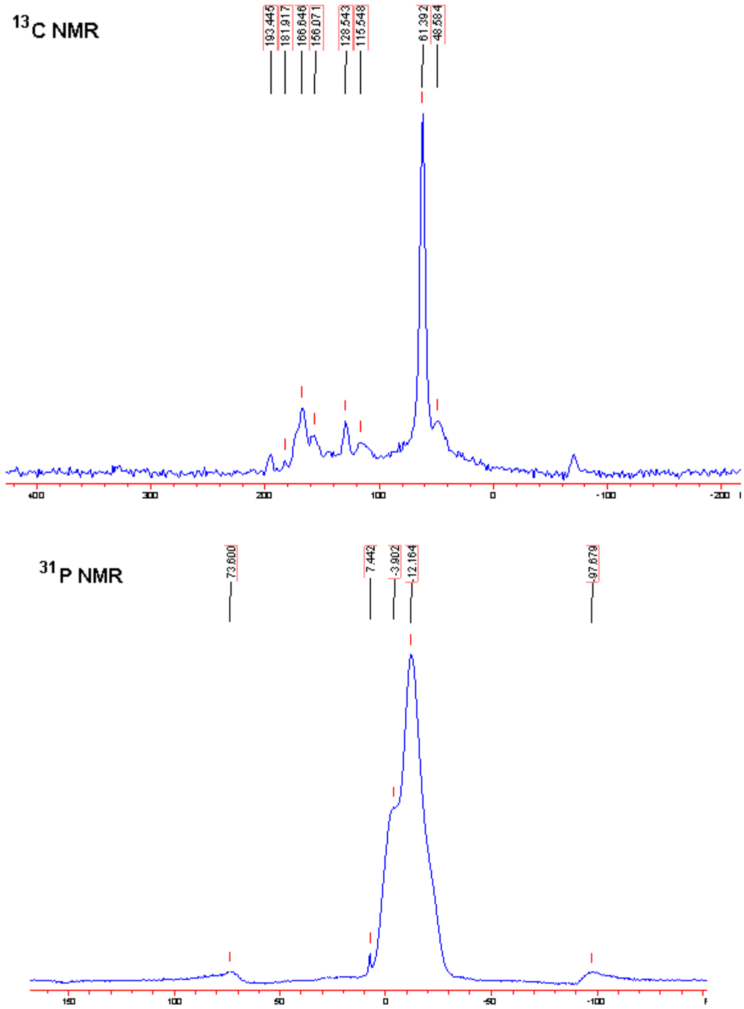
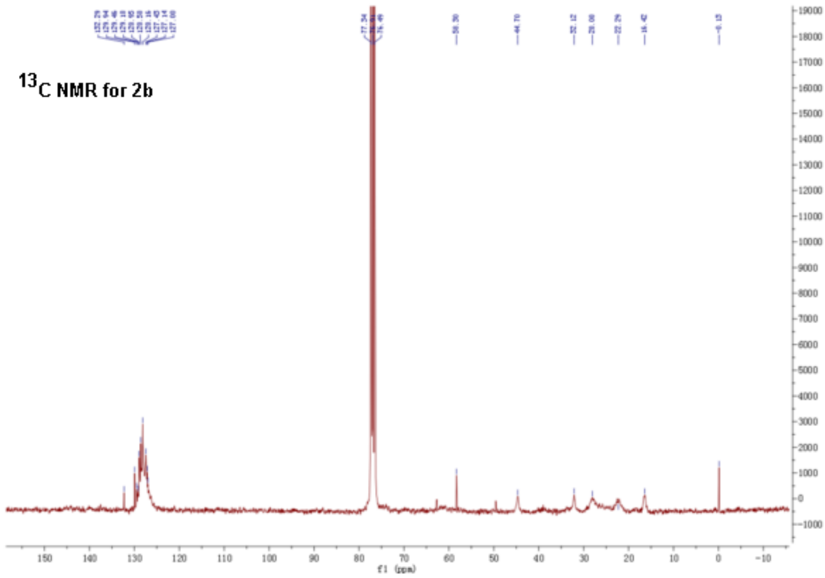


Figure S6. The solid state ^{13}C NMR and ^{31}P NMR of zirconium phosphonate **2b**

3. The solution ^{13}C and ^{31}P NMR of compounds **2b** and **2c** (**Figure S7-S8**)



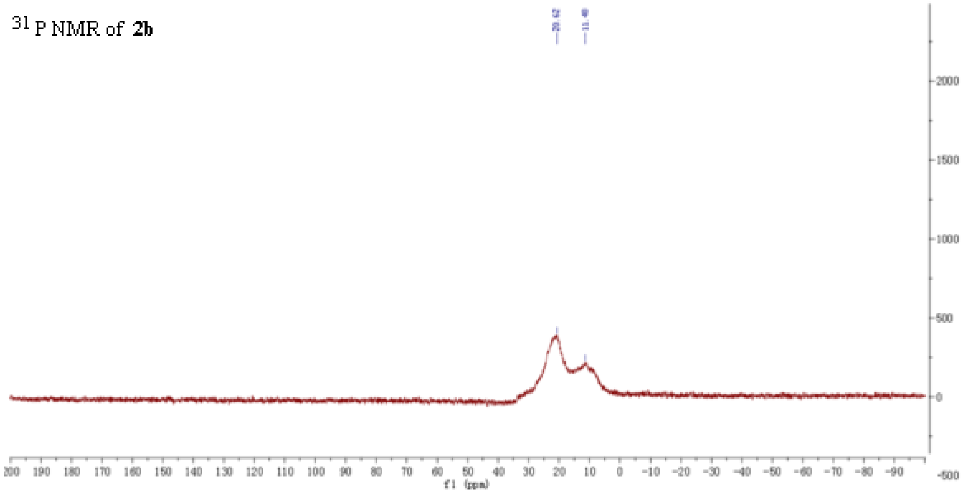


Figure S7. The solution ^{13}C NMR and ^{31}P NMR of zirconium phosphonate **2b**

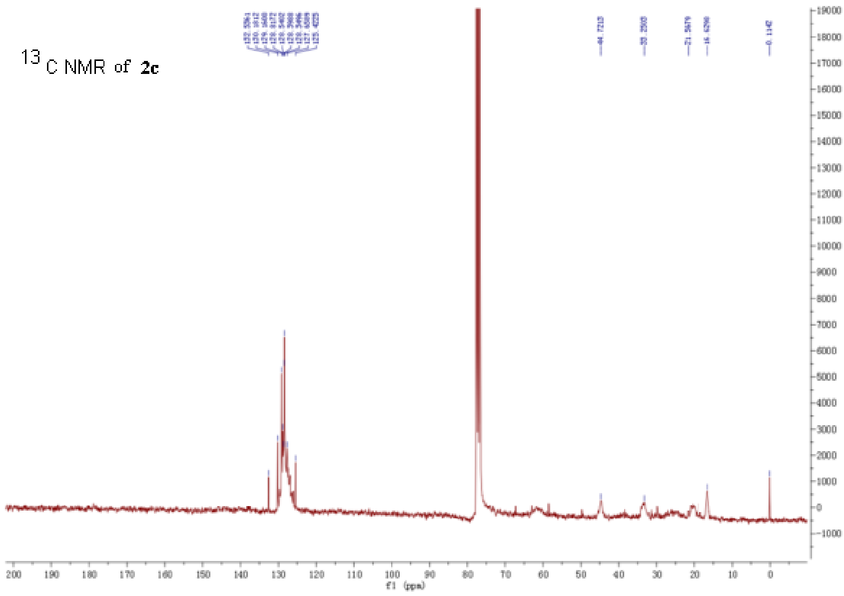


Figure S7. The solution ^{13}C NMR of zirconium phosphonate **2c**

4. The thermogravimetric curves of the other supports and their supported ruthenium catalysts (**Figure S9-S12**)

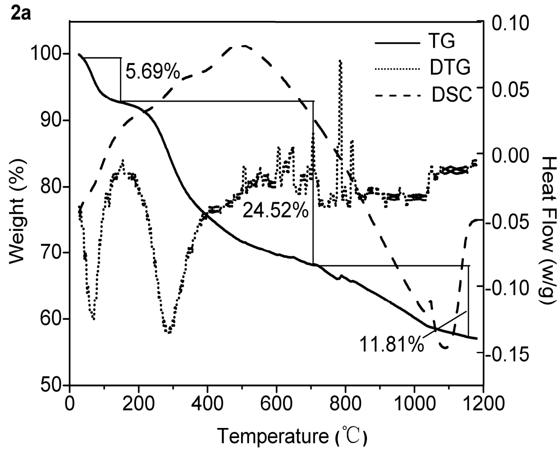


Figure S9. The thermogravimetric curves of the support **2a**

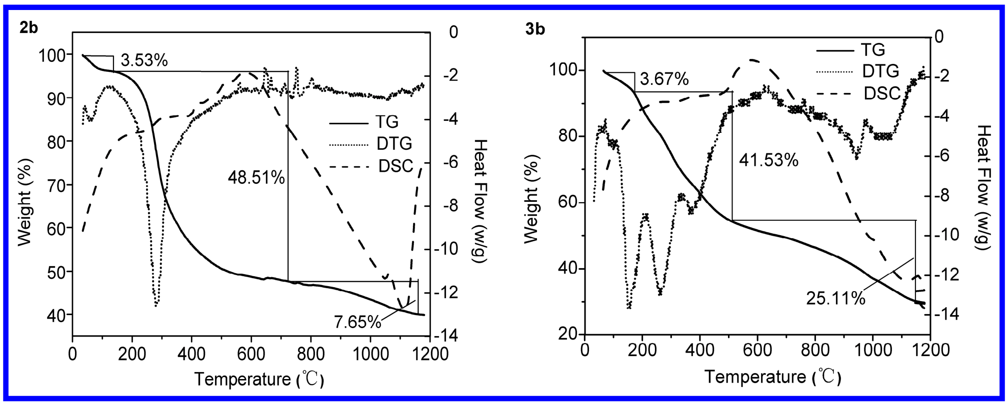


Figure S10. The thermogravimetric curves of the support **2b** and its supported catalyst **3b**

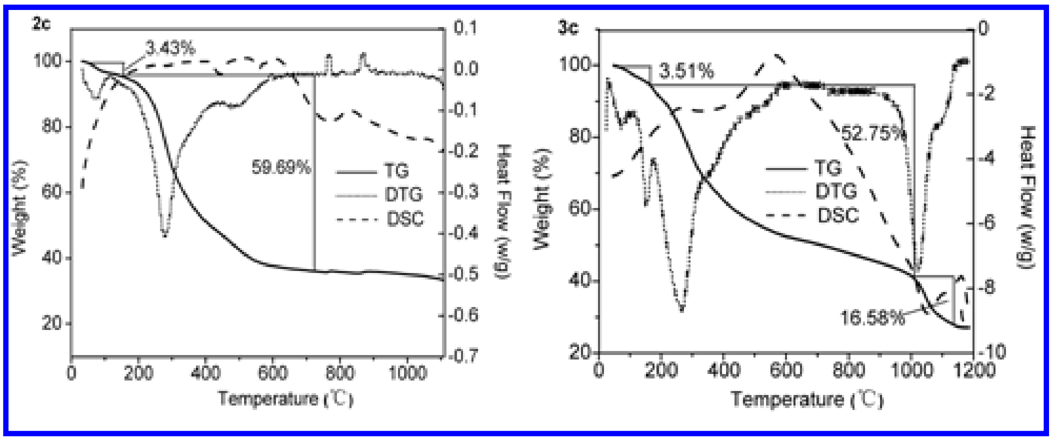


Figure S11. The thermogravimetric curves of the support **2c** and its supported ruthenium catalyst

3c

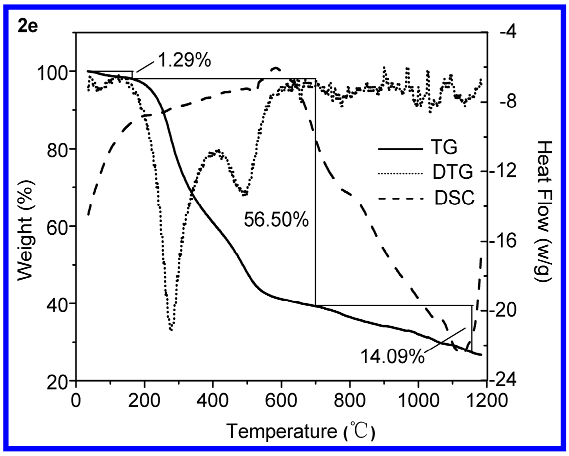


Figure S12. The thermogravimetric curves of the support **2e**

5. Isotherms and distributions of pore diameter of the other supports and their supported ruthenium catalysts (**Figure S13-S17**)

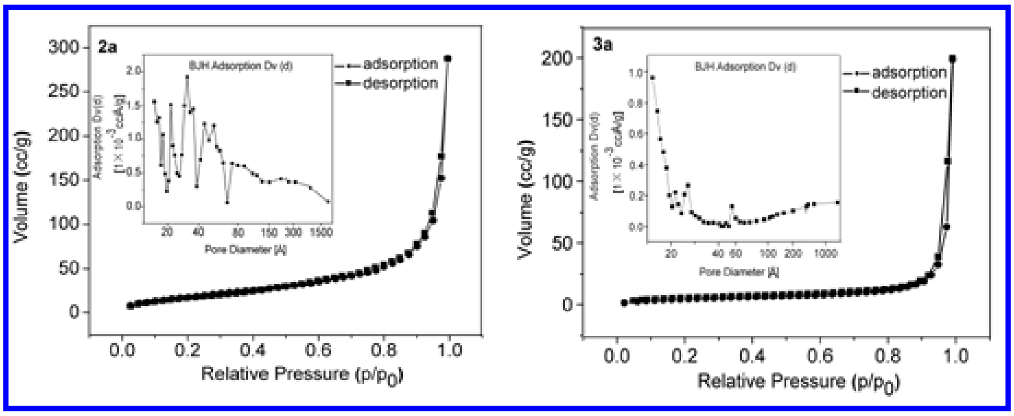


Figure S13. Isotherms and distributions of pore diameter of support **2a** and its supported ruthenium catalyst **3a**

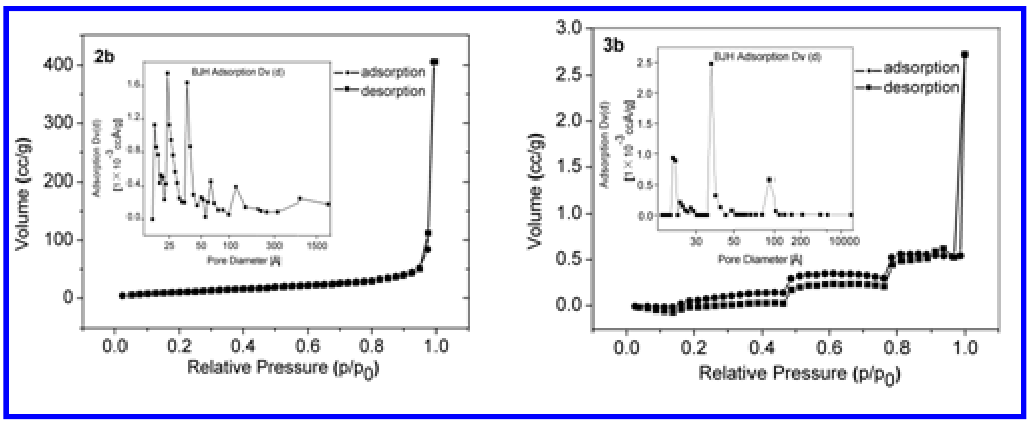


Figure S14. Isotherms and distributions of pore diameter of support **2b** and its supported ruthenium catalyst **3b**

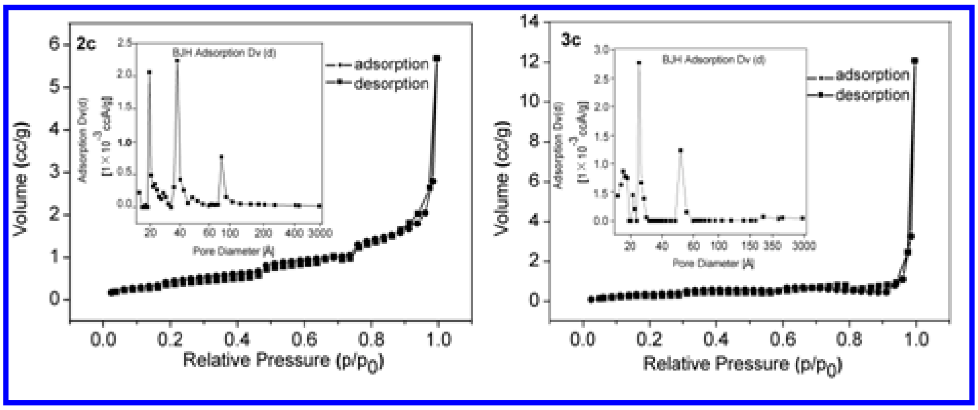


Figure S16. Isotherms and distributions of pore diameter of support **2c** and its supported ruthenium catalyst **3c**

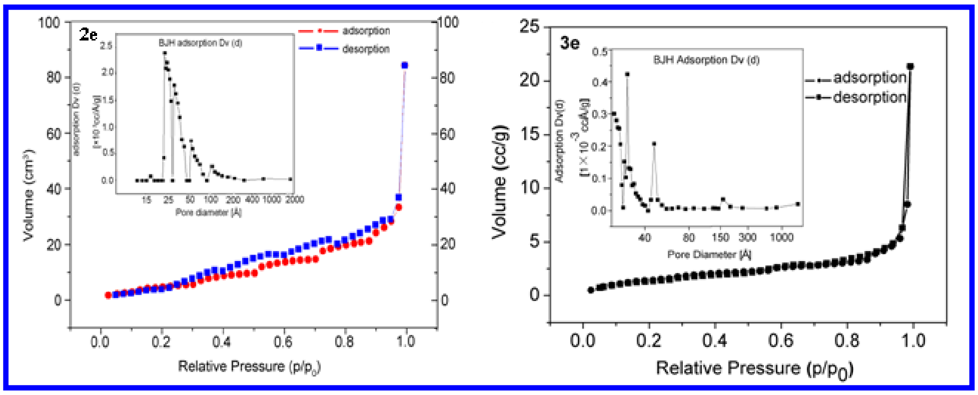
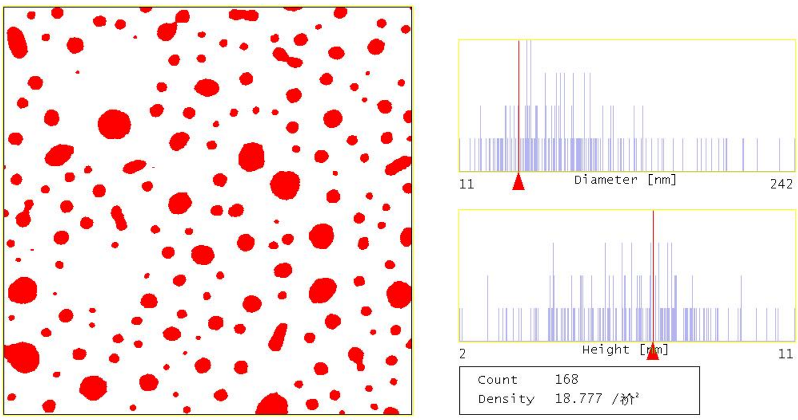


Figure S17. Isotherms and distributions of pore diameter of support **2e** and its supported ruthenium catalyst **3e**

6. Particle analysis picture of **2a** (**Figure S18**)



	Mean	Minimum	Maximum	Sigma
Height	6.668 nm	2.186 nm	11.158 nm	1.748 nm
Area	7669.0 nm²	103.00 nm²	46142 nm²	8361.5 nm²
Diameter	87.817 nm	11.452 nm	242.39 nm	45.305 nm
Length	105.43 nm	18.529 nm	302.43 nm	57.994 nm
Width	75.750 nm	8.286 nm	226.23 nm	40.336 nm

Figure S18. The particle analysis picture of **2a**: scan scale 3000nm×3000nm, scan rate:1.40Hz

5. The diameter of the particles (**Table ST1**) and the height of the particles ranges (**Table ST2**)

Table ST1. The diameter distribution of particles **2a**

Diameter	number
11-30	6
30-50	15
50-70	40
70-90	30
90-110	32
110-130	16
130-150	10
150-170	5
170-195	5
195-210	4
210-230	3

Table ST2. The height of particle **2a** ranges

Height (nm)	number
1.0-2.0	3
3.0- 4.0	2
4.0-5.0	9
5.0-6.0	18
6.0-7.0	25
7.0-8.0	29
8.0-9.0	43
9.0-10.0	26
10.0-11.0	7
11.0-13.0	6

7. Composition of as-prepared zirconium phosphonate nanocomposites (**Table ST3**)

Table ST3. The organic weight loss, x and y values of zirconium phosphonates **2a-e** bearing different arm lengths (n)

n	**2**	**3**	**4**	**5**	**6**
Water weight loss(%)	5.69	3.53	3.43	2.50	1.29
organic weight loss (%)	36.33	56.16	59.69	67.36	70.59
x value	0.44	0.95	1.00	1.37	1.50

y value	1.11	1.83	1.14	1.07	0.60

Based on the data of thermogravimetric analysis (TGA) and zirconium phosphonate **2b** as an example, the above values were calculated as follows: the 3.53 % weight loss was observed below 180 ºC, which illustrated the presence of adsorbed interlayer water. The end product of the thermal reaction at 1200 ºC is zirconium pyrophosphate (Formula Weight= 266.2), and the organic weight loss in the temperature 180-1200 ºC range was 56.16 %. The value of *x* in the formula $Zr(OH)_{4-2x}(O_3PR)_x$ was determined from eq 1 and eq 2.

$$\begin{cases} \dfrac{\text{The theoretic water weight loss}}{\text{Formula weight}} = (W_{25^\circ C} - W_{180^\circ C})\ \% & (1) \\ \dfrac{\text{The theoretic organic weight loss}}{\text{Formula weight}} = (W_{180^\circ C} - W_{1200^\circ C})\ \% & (2) \end{cases}$$

Combined with the formula of **2b**, eq 3 and eq 4 were obtained.

$$\frac{18y}{403x+18y+159.25} = 3.53\% \qquad (3)$$

$$\frac{372x-30}{403x+18y+159.25} = 56.16\% \qquad (4)$$

Then, x=0.95, y=1.83 . The other x, y values were calculated according to the same method.