Polypyrrole (PPy), as one of the conducting polymers, has aroused wide interests because of its excellent architectural diversity and flexibility, high electrical conductivity, environmental stability, relatively low densities and ease of low cost synthesis\(^1,2\). Multifunctional PPy nanostructures have been synthesized by the oxidation of pyrrole (Py) to form PPy on the surface of electrical, magnetic and optical inorganic nanoparticles. Some PPy/metal oxide composites have already been reported in the literature. In comparison with neat materials, mixed composites exhibit improvement in the chemical and physical properties, such as photoactivity and electronic transfer\(^3\). On the basis of these properties, important applications have been reported as sensors\(^4\), photocatalysts\(^3\) and battery anodes\(^5,6\). However, another important property, its excellent adsorption ability is usually neglected by researchers.

A microemulsion is a thermodynamically stable, isotropic, optically transparent solution consisting of water, oil and a surfactant\(^7,8\). Microemulsion can co-solubilize large amounts of hydrophilic and hydrophobic compounds, which may resolve the well-known solubilization problems\(^9,10\). An approach to create tunable reaction media for chemical processes is the use of surfactants in aqueous solutions. Water can act as a solvent for water-soluble catalysts, but in the case of hydrophobic reactants, it has the disadvantage of poor reactant solubility. The addition of surfactant results in an increase of the solubility of non-polar reactants in the polar water phase, thus reducing the miscibility gap in the phase diagram. Furthermore, the surfactant reduces the interfacial tension and increases the interfacial area between both phases\(^11,12\). This method has been widely employed for the preparation of metal nanoparticles with different sizes. However, to the best of our knowledge, use of microemulsions as a chemical reaction medium for the selective hydrogenation of unsaturated aldehyde has not been reported until now.

Selective hydrogenation of \(\alpha,\beta\)-unsaturated aldehyde at the carbonyl (C=O) and olefinic (C=C) group is an important reaction, because most products are important intermediates for the syntheses of many chemicals\(^13,14\). Cinnamaldehyde (CAL) is a particularly important representative of \(\alpha,\beta\)-unsaturated aldehyde. Its two partial hydrogenation products, hydrocinnamaldehyde (HCAL) and cinnamyl alcohol (COL), are important intermediates in the manufacture of chemicals (particularly perfumes, flavors, and pharmaceuticals)\(^15,16\). In the reaction pathways for the hydrogenation of CAL, HCAL and COL can be
selectively obtained by choosing a suitable reaction medium and metal complex catalyst. However, while focus of earlier studies has been mainly on suitable promoters, supports, metals and reduction conditions\textsuperscript{17}, the problem of C=O bond enrichment on the surface of the catalyst has not been addressed as yet. Hence, herein PPy/metal oxide composite as catalyst support and microemulsion medium were employed in the hydrogenation reaction to increase the opportunity for C=O bond enrichment on the surface of the catalyst.

In this article, we have synthesized PPy/ZrO$_2$ nanocomposite in a simple method and prepared Ru based bimetallic catalysts using the nanocomposite as metal catalyst support. Different metals X (Co, Ni, Mn) were used as promoter and the content of Ru and metal was 0.50 wt% and 0.30 wt%, respectively. The catalysts were prepared through the three steps formation process shown in Scheme 1. Firstly, ZrO$_2$ nanoparticles were synthesized by sol-gel method, and then PPy/ZrO$_2$ was obtained through the \textit{in situ} polymerization of pyrrole (Py) in the suspension of ZrO$_2$ initiated by Fe$^{3+}$. Finally, RuX nanoparticles were deposited onto the surface of PPy/ZrO$_2$ nanocomposites. The catalytic activity of RuX/ZrO$_2$ and RuX/PPy/ZrO$_2$ was investigated under single ethanol medium in microemulsion medium.

Materials and Methods

Catalysts preparation

ZrO$_2$ nanoparticles was prepared by sol-gel method via sol-gel formation, evaporation of water and calcination process. Zirconium nitrate (0.17 mol, AR, Aladdin) and citric acid (0.17 mol, AR, Aladdin) were dissolved separately in water (200 mL and 500 mL respectively). Then citric acid solution was added drop-wise to the continuously stirred zirconium nitrate solution in a 1 L beaker. The solution became milky white sol gradually and eventually turned clear and colorless. Stirring was continued for 0.5 h, and then the solution was kept undisturbed for 1 h. The solution was heated to boil to evaporate the water until a reddish-yellow sticky liquid was formed. The liquid was dried at 110 °C overnight to form a spumous fluffy solid. The solid was calcined at 500 °C for 2 h and subsequently at 650 °C for another 1.5 h. A resulting white ZrO$_2$ powder was obtained. PPy was formed on the surface of ZrO$_2$ by polymerization of Py in a solution containing FeCl$_3$ (AR, Aladdin). The detailed procedure was as follows: 50 mL of deionized water, 0.5 g of sodium dodecylbenzene sulphonate (AR, Aladdin), 0.2 mL of Py (AR, Aladdin) and 1 g of ZrO$_2$ were added to a flask with stirring. When a homogeneous suspension was formed, 20 mL of aqueous solution of FeCl$_3$·6H$_2$O (0.1 g/mL) was added drop-wise to the suspension which was then stirred at room temperature for 1 h. PPy/ZrO$_2$ powder was recovered by filtering and dried at 60 °C. Ru based catalysts supported on ZrO$_2$ and PPy/ZrO$_2$ were prepared by the conventional impregnation method with NaHB$_4$ as reductant.

Catalyst characterization

X-ray diffraction (XRD) patterns were recorded at room temperature using a Bruker D8 Advance X-ray diffractometer with the Cu-K$_\alpha$ radiation at 40 kV and 30 mA. The surface functional groups in lignin were identified by FT-IR recorded on a Thermo Scientific Nicolet 380 spectrometer. The samples were dispersed in KBr matrix (1:100), followed by an appropriate compression to form pellets. For each sample, the spectrum was investigated in absorbance units over a spectral range of 4000–400 cm$^{-1}$ at a spectral resolution of 4 cm$^{-1}$ and 32 scans. The background (measured in air) was subtracted from the FT-IR spectra. TEM were obtained with a FEI Tecnai G20 TEM instrument fitted with a CCD794 camera, operating at an accelerating voltage of 200 kV. For TEM studies, the sample was suspended in ethanol with a few drops of 2-dimethylaminoethanol used as a dispersant, and the ethanol suspension was deposited straight away on a carbon film supported on a copper grid prior to analysis.

XPS was measured with a K-Alpha XPS medium (Thermo Fisher Scientific, USA) using monochromatic Al K$\alpha$ as the excitation source. Survey (wide) scans spanned from 1000 to 0 eV binding energy, which were collected with an analyzer pass energy of 100 eV at an interval of 1.00 eV.
Hydrogenation reaction

The hydrogenation reactions were carried out in a stainless autoclave reactor with a 50 mL Teflon sleeve. In a typical procedure, 0.5 g catalyst was dispersed in 19 mL ethanol and then 8.2 mmol CAL was added to the solution. The reactor was sealed, purged with H$_2$ three times and then pressurized to 2.0 MPa. The reaction was conducted at 70°C with a stirring speed of 750 rpm for 2 h. The hydrogenation reactions were carried out at the same conditions in oil-in-water (O/W) microemulsion mediums comprising ethanol, water, CAL and stabilized by different surfactants, namely, DTAB and Tween 80. The reaction mixture was analyzed by Shimadzu GC-2010 gas chromatograph with a flame ionization detector (FID) medium equipped with a capillary column SE-54 (5%phenyl-95% dimethylpolysiloxane: 30 m×0.32 mm×0.5 µm).

Results and Discussion

Catalyst characterization

The XRD patterns of the ZrO$_2$ and PPy/ZrO$_2$ support and supported catalysts are shown in Fig. 1. In the XRD pattern of ZrO$_2$, the sharp diffraction peaks of the ZrO$_2$ nanoparticles imply that the ZrO$_2$ was crystalline in nature. The strong peaks at 2θ = 30.3°, 35.2°, 50.4°, 60.2° are observed, which correspond well to (011), (110), (112), (121) planes of pure tetragonal ZrO$_2$ (JCPDS card 50-1089), respectively. Other weak peaks at 24.0°, 28.2°, 31.5°, 34.2° belong to the (110), (-111), (111), (200) planes of pure monoclinic ZrO$_2$ (JCPDS card 37-1484)\(^1\). Peaks for impurities are not observed. This indicates that both tetragonal and monoclinic phase exist in the ZrO$_2$ calcined at 650°C and the main phase was tetragonal. The crystallite size for ZrO$_2$ estimated from the Scherrer formula ($D_{\text{hkl}} = \frac{K\lambda}{β\cosθ}$) is found to be 16.5 nm. In the XRD pattern of PPy/ZrO$_2$, the typical diffraction peaks of monoclinic ZrO$_2$ disappear, which along with the clear decrease in intensity of the diffraction peaks of tetragonal ZrO$_2$ indicates the formation of PPy on the surface of ZrO$_2$ \(^2\) and the change of chemical structure of ZrO$_2$ particles. Furthermore, the XRD pattern of PPy/ZrO$_2$ shows the absence of any new sharp diffraction line compared with ZrO$_2$, indicating that the deposited PPy was amorphous. The XRD characteristic peaks corresponding to metal species (Ru, Ni, Co) is not present for ZrO$_2$ and PPy/ZrO$_2$ supported catalysts, due to the high dispersion of the amorphous metal particles, and probably, the very low intensity of the metal peaks compared to the crystallite size of the ZrO$_2$. However, there is a slight decrease in the intensity of the peaks of ZrO$_2$ supported catalysts as compared with that of the bare ZrO$_2$, probably due to the formation of metal particles onto the surface of ZrO$_2$ nanoparticles.

Figure 2 shows the FTIR spectra of ZrO$_2$ and PPy/ZrO$_2$ support and supported catalysts recorded from 2000–400 cm$^{-1}$. In the FTIR spectrum of ZrO$_2$, the peak at 1636 cm$^{-1}$ attributed to the O-H vibration of free H$_2$O absorbed in the ZrO$_2$ sample\(^3\). Characteristic bands ascribed to ZrO$_2$ are at 416, 494 and 573 cm$^{-1}$

![Fig. 1 — XRD pattern of the ZrO$_2$ and PPy/ZrO$_2$ support and supported catalysts.](image1)

![Fig. 2 — FT-IR spectra of (1) ZrO$_2$, (2) PPy, (3) PPy/ZrO$_2$, (4) Ru/ZrO$_2$, (5) RuCo/ZrO$_2$, (6) RuNi/ZrO$_2$, (7) Ru/PPy/ZrO$_2$, (8) RuCo/PPy/ZrO$_2$, and (9) RuNi/PPy/ZrO$_2$.](image2)
due to the Zr-O vibrations. In the FT-IR spectrum of 
Ppy, the peaks of free H2O are not seen.

It was observed that the spectrum of PPy/ZrO2 was 
combined with that of PPy from 2000–750 cm⁻¹ and 
with that of ZrO2 from 750–400 cm⁻¹. The bands of 
PPy/ZrO2 sample from 750–400 cm⁻¹ was slightly 
decreased in intensity in comparison with those of 
bare ZrO2. Compared with the individual polymer 
spectrum, the blue shift and the decrease of some 
peaks in the corresponding composite spectrum may 
be due to the coordination of N atom in the pyrrole 
ring and the Zr atom in ZrO2 nanoparticles. This result 
is indicative of a strong chemical interaction between 
PPy polymer and ZrO2, rather than a physical blend of 
the two components. This conclusion is consistent 
with that of XRD pattern analysis. There was no 
difference between the FTIR spectra of ZrO2 
supported catalysts and bare ZrO2, which may be 
because metal nanoparticles had no response in 
infrared region. However, there was an intense 
interaction between metal nanoparticles and PPy, 
which resulted in a shift, decrease and disappearance 
of some peaks. According to Mo et al. in the 
inorganic nanoparticles polymer composites, the 
intercalation of the inorganic nanoparticles will 
change the electron density of the polymer chain, 
leading to shift of the corresponding absorption peak 
of functional groups in polymer. Also, the direction 
of shift is closely related to the type of the polymer.

The size and morphology of the samples are shown 
by TEM and high resolution TEM (Fig. 3). The bare 
ZrO2 was composed of irregular-shape particles with 
a size of 100–400 nm, and every particle consisted of 
crystallites with a diameter ~10—20 nm (Fig. 3b). 
This agrees well with the crystallite size (16.5 nm) 
estimated by the Scherrer formula from the XRD 
peaks. In the HRTEM mode, it was possible to 
measure the spacing of the well resolved interference 
fringes (Fig. 3a). The measured interplanar spacing 
(d = 2.947, 2.836, 3.672 Å) was in good agreement 
with the value for the (011)-planes of the tetragonal 
structure and the (111)-planes and (110)-planes of the 
monoclinic phase. The HRTEM of RuCo/ZrO2 
prepared by the impregnation method is shown in 
Fig. 3d. It can be seen that RuCo nanoparticles of 
different sizes were uniformly coated on the surface 
of ZrO2 particles. From Fig. 3e, it can be observed 
that complete PPy coating was formed on the surface 
of ZrO2 particles, and metal nanoparticles were 
dispersed on the PPy.

Fig. 3 — High resolution TEM of (a) ZrO2, TEM of (b) ZrO2, (c) PPy/ZrO2, (d) RuCo/ZrO2, and, (e) RuCo/PPy/ZrO2.
To obtain information about the chemical environment and atomic concentrations presented in catalysts, XPS analysis was performed. Figure 4 shows a typical XPS survey spectrum of ZrO$_2$ and PPy/ZrO$_2$ supported catalysts. The results reveal the obvious differences between the two kinds of catalysts. The major difference was that the intensity of C1s peak increased sharply and the peak of Zr3d decreased due to the formation of PPy. In addition, no Fe element was detected in PPy/ZrO$_2$ supported catalysts, which indicates that FeCl$_3$ was washed clean without any residual during the PPy/ZrO$_2$ preparation. Figure 5 shows the Ru3d XPS spectra of the Ru based catalysts. Since the Ru3d$_{5/2}$ peak overlapped with the C1s peak of PPy and contaminant carbon, only the Ru3d$_{5/2}$ peak was considered to determine the chemical state of Ru. It was found that the Ru species in all the catalysts existed mainly in the metallic state with the Ru3d$_{5/2}$ binding energy of 280.1 eV. In addition, some RuO$_2$ was detected in all the catalysts. The formation of some RuO$_2$ on the surface of catalysts may result in a broadening of the spectrum of the Ru-based catalyst.

**Hydrogenation reaction**

In order to investigate the detailed catalytic performance of PPy/ZrO$_2$ supported catalysts, we compared the catalytic hydrogenation results under the same reaction conditions and results are listed in Table 1. The hydrogenation of CAL typically produced a mixture of the desired COL and HCAL and the undesired hydrocinnamyl alcohol (HCOL). Aldol condensation product of acetal (ACE) and other unidentified products may be produced in small amounts particularly over non-selective catalysts$^{22}$. Among the catalysts tested, the best conversion (78.2%) was observed in the presence of RuMn/PPy/ZrO$_2$, and a high selectivity in COL (70.4%) was achieved simultaneously. The best selectivity of COL (75.4%) was achieved in the presence of RuCo/PPy/ZrO$_2$. It is obviously that the
C=O hydrogenation can be improved by Co-doped catalysts. On the other hand, Ni-doped catalysts showed high selectivity in HCAL which demonstrated that the hydrogenation of the C=O group is normally favored over Ni-doped catalysts. It may be noted that in the presence of PPy/ZrO2 supported catalysts, conversions of COL were always higher than those obtained with the corresponding bare ZrO2 supported catalysts and there was no yield of by-product of ACE. This may be because of the excellent electrical conductivity and adsorption properties of PPy.

Earlier studies have indicated that the adsorption property of PPy/metal oxide is exhibited through electrostatic interaction or ion exchange, largely due to the existence of positively charged nitrogen atoms in PPy matrix. Metal ions and some organic molecules can be adsorbed through the change of PPy surface charges. For example, PPy/Fe3O4 magnetic nanocomposite was used to adsorb and remove toxic Cr (VI) in waste water. In this work, metal ions were adsorbed on the surface of support and reduced in the process of catalyst preparation, which can improve the content and dispersion of metal nanoparticles in catalyst. Therefore, the PPy in the composite not only increases the thermal stability and conductivity of inorganic nanoparticles, but also provides an efficient matrix for the introduction of metal nanoparticles. The special structure enhances the interaction between ZrO2 and metal nanoparticles through the PPy polymer bridge, which endows the composite with excellent catalytic activity.

For the reaction catalyzed by RuX/PPy/ZrO2, the unsaturated aldehydes are adsorbed on the PPy/ZrO2 because the oxygen atom of the C=O group forms weaker hydrogen bond with the hydrogen atom of C-H or N-H in PPy, which makes the density of C=O group on the PPy/ZrO2 surface higher than that on bare ZrO2. Then, the activated C=O group is attacked by the hydrogen activated over RuX alloy surface. Considering the space effect, the high dispersion of metal nanoparticles favors C=O bond hydrogenation. A small RuX domain decreases the opportunity to interact with C=C bond, preventing the hydrogenation of the C=C bond. Hence, catalyst supported on PPy/ZrO2 presents high conversion and good selectivity for COL.

The CAL hydrogenation properties over PPy/ZrO2 supported catalysts in different microemulsion mediums were also studied and the results are listed in Table 2. It can be seen that microemulsion medium results in a significant improvement in the CAL conversion and COL selectivity, compared to the reaction medium of only pure ethanol. Fanun et al. have reported that the special microenvironment of the microemulsion interfacial film is similar to a micellar microenvironment that can reduce the activation energy of some reactions, and this plays a catalytic effect on the reaction and increases the reaction rate. The microemulsion interfacial film is similar to the activity center of enzymes which can

### Table 1 — Hydrogenation of CAL over ZrO2 and PPy/ZrO2 supported Ru based bimetallic catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conv. (%)</th>
<th>TOFb</th>
<th>HCAL (%)</th>
<th>HCOL (%)</th>
<th>COL (%)</th>
<th>ACE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru/ZrO2</td>
<td>11.0</td>
<td>0.30</td>
<td>38.4</td>
<td>2.2</td>
<td>31.7</td>
<td>27.7</td>
</tr>
<tr>
<td>Ru/PPy/ZrO2</td>
<td>59.2</td>
<td>1.64</td>
<td>21.7</td>
<td>5.7</td>
<td>72.6</td>
<td>0.0</td>
</tr>
<tr>
<td>RuNi/ZrO2</td>
<td>22.0</td>
<td>0.61</td>
<td>85.9</td>
<td>2.4</td>
<td>7.2</td>
<td>4.5</td>
</tr>
<tr>
<td>RuNi/PPy/ZrO2</td>
<td>77.6</td>
<td>2.14</td>
<td>44.0</td>
<td>8.1</td>
<td>47.9</td>
<td>0.0</td>
</tr>
<tr>
<td>RuCo/ZrO2</td>
<td>15.0</td>
<td>0.41</td>
<td>47.5</td>
<td>0.0</td>
<td>47.1</td>
<td>5.4</td>
</tr>
<tr>
<td>RuCo/PPy/ZrO2</td>
<td>45.4</td>
<td>1.25</td>
<td>20.2</td>
<td>4.4</td>
<td>75.4</td>
<td>0.0</td>
</tr>
<tr>
<td>RuMn/ZrO2</td>
<td>8.3</td>
<td>0.23</td>
<td>41.0</td>
<td>3.6</td>
<td>29.5</td>
<td>16.9</td>
</tr>
<tr>
<td>RuMn/PPy/ZrO2</td>
<td>78.2</td>
<td>2.16</td>
<td>21.8</td>
<td>7.8</td>
<td>70.4</td>
<td>0.0</td>
</tr>
</tbody>
</table>

aReact. cond.: CAL: 8.2 mmol, C2H5OH: 19.0 mL, temp.: 70 °C, pressure: 2.0 MPa, time: 2.0 h.
bTOF: CAL (mol)/Ru (mol)/min. calc. from the amount of CAL conversion.
cACE: acetals.

### Table 2 — The hydrogenation of the CAL in different microemulsion mediums

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Microemulsion medium</th>
<th>Conv. (%)</th>
<th>TOF</th>
<th>HCAL (%)</th>
<th>HCOL (%)</th>
<th>COL (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru/PPy/ZrO2</td>
<td>DTAB/ethanol/water</td>
<td>91.5</td>
<td>2.53</td>
<td>12.4</td>
<td>11.0</td>
<td>76.6</td>
</tr>
<tr>
<td></td>
<td>Tween80/ethanol/water</td>
<td>59.1</td>
<td>1.63</td>
<td>14.3</td>
<td>5.3</td>
<td>80.3</td>
</tr>
<tr>
<td>RuNi/PPy/ZrO2</td>
<td>DTAB/ethanol/water</td>
<td>99.1</td>
<td>2.74</td>
<td>13.8</td>
<td>33.0</td>
<td>53.2</td>
</tr>
<tr>
<td></td>
<td>Tween80/ethanol/water</td>
<td>96.6</td>
<td>2.67</td>
<td>43.1</td>
<td>29.3</td>
<td>27.6</td>
</tr>
<tr>
<td>RuCo/PPy/ZrO2</td>
<td>DTAB/ethanol/water</td>
<td>93.5</td>
<td>2.58</td>
<td>10.2</td>
<td>13.6</td>
<td>76.2</td>
</tr>
<tr>
<td></td>
<td>Tween80/ethanol/water</td>
<td>62.0</td>
<td>1.71</td>
<td>16.4</td>
<td>5.4</td>
<td>78.2</td>
</tr>
<tr>
<td>RuMn/PPy/ZrO2</td>
<td>DTAB/ethanol/water</td>
<td>95.3</td>
<td>2.63</td>
<td>16.6</td>
<td>15.4</td>
<td>68.0</td>
</tr>
<tr>
<td></td>
<td>Tween80/ethanol/water</td>
<td>83.4</td>
<td>2.30</td>
<td>17.2</td>
<td>10.6</td>
<td>72.2</td>
</tr>
</tbody>
</table>

aReact. cond.: CAL: 8.2 mmol, temp.: 70 °C, pressure: 2.0 MPa, time: 2.0 h.
bWater-to-surfactant (W/S) mass ratio: 5, to form O/W microemulsion medium.
bring the reaction substrate into a certain arrangement and orientation, in the O/W microemulsion medium. The polarity part, namely carbonyl, is inserted into the water to be adsorbed on the PPy/ZrO$_2$ to form weaker hydrogen bond of C-H or N-H in PPy as shown in Fig. 6. Hence, the O/W microemulsion structured fluids can improve the selective hydrogenation of C=O due to the orientation of reactants at the interfacial region.

**Conclusions**

PPy/ZrO$_2$ nanocomposite was successfully prepared and used as catalyst support for the hydrogenation reaction of CAL for the first time. The adsorption property of PPy was used to facilitate dispersion of metal catalysts and increase the concentration of unsaturated aldehydes. The advantage of microemulsion medium was also employed in the hydrogenation reactions. The catalysts supported on PPy/ZrO$_2$ showed a higher hydrogenation activity than that supported on ZrO$_2$ due to the excellent adsorption property of PPy/ZrO$_2$. Also, catalysts in microemulsion medium presented a higher activity in terms of CAL conversion and COL selectivity as compared with the previously reported ethanol medium.

**Acknowledgement**

The authors gratefully acknowledge financial support from the National Natural Science Foundation of China (No. 21203113), PR China.

**References**