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AgAuPd/meso-Co₃O₄: High-performance catalysts for methanol oxidation

Jun Yang, Yuxi Liu *, Jiguang Deng, Xingtian Zhao, Kunfeng Zhang, Zhuo Han, Hongxing Dai #

Beijing Key Laboratory for Green Catalysis and Separation, Key Laboratory of Beijing on Regional Air Pollution Control, Key Laboratory of Advanced Functional Materials, Education Ministry of China, Laboratory of Catalysis Chemistry and Nanoscience, Department of Chemistry and Chemical Engineering, College of Environmental and Energy Engineering, Beijing University of Technology, Beijing 100124, China

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ABSTRACT

The meso-Co₃O₄ and Ag_{0.75}Au_{1.14}Pd/meso-Co₃O₄ catalysts were prepared using the KIT-6-templating and polyvinyl alcohol-protected NaBH₄ reduction methods, respectively. Various techniques were used to characterize physicochemical properties of these materials. Catalytic performance of the samples was evaluated for methanol combustion. The cubically crystallized Co₃O₄ support displayed a three-dimensionally ordered mesoporous structure. The supported noble metal nanoparticles (NPs) possessed a surface area of 115–125 m²/g, with the noble NPs (average size = 2.8–4.5 nm) being uniformly dispersed on the surface of meso-Co₃O₄. Among all of the samples, 0.68 wt% Ag_{0.75}Au_{1.14}Pd/meso-Co₃O₄ showed the highest catalytic activity ($T_{50\%} = 100\text{ }^{\circ}\text{C}$ and $T_{90\%} = 112\text{ }^{\circ}\text{C}$ at a space velocity of 80000 mL (g⁻¹ h⁻¹). The partial deactivation of the 0.68 wt% Ag_{0.75}Au_{1.14}Pd/meso-Co₃O₄ sample due to water vapor or carbon dioxide introduction was reversible. It is concluded that the good catalytic performance of 0.68 wt% Ag_{0.75}Au_{1.14}Pd/meso-Co₃O₄ was associated with its highly dispersed Ag_{0.75}Au_{1.14}Pd alloy NPs, high adsorbed oxygen species concentration, good low-temperature reducibility, and strong interaction between Ag_{0.75}Au_{1.14}Pd alloy NPs and meso-Co₃O₄.

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1. Introduction

VOCs are major contributors to ozone and photochemical smog, which lead to air pollution and human being's sickness [1]. Methanol is one of the VOCs and widely used as solvents, fuels for specialized vehicles or feedstock for manufacturing of other value-added chemicals [2,3]. Furthermore, methanol is highly toxic and harmful to human health. Hence, it is essential to develop practical and cost-effective methods to control the emission of methanol. Up to now, the most efficient technology for VOC elimination is the catalytic combustion, which pos-

sesses a number of advantages, such as high efficiency, low light-off temperature, simple equipment, and no secondary pollution [4,5]. The key point is to choose effective catalysts with high performance.

Supported noble metals (especially Pd) have been considered as the most popular catalysts used for VOCs combustion due to their high performance at low temperatures [6,7]. Nevertheless, the presence of moisture can be the adverse factor influencing the activity of a supported noble metal catalyst [8]. Noble metal alloy catalysts were reported to possess activities superior to those of their single-component counterparts, and

* Corresponding author. Tel: +86-10-67396118; Fax: +86-10-67391983; E-mail: yxliu@bjut.edu.cn

Corresponding author. Tel: +86-10-67396118; Fax: +86-10-67391983; E-mail: hxdai@bjut.edu.cn

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the former also displayed better thermal stability and poison-resistant ability than the latter. For example, Wei and coworkers reported that the AuPd/3DOM-TiO₂ [9], PtRu/TiO₂ [10], and Pd_xCo_{3-x}O₄/3DOM Ce_{0.2}Zr_{0.8}O₂ [11] catalysts were active for the photocatalytic reduction of CO₂ and soot combustion. Calzada et al. [1] found that the Ru-Au/TiO₂ catalyst performed better than the supported Ru or Au counterpart at low temperatures (< 50 °C) in the total oxidation of methanol. Wang et al. [12] reported that the 0.96AuPd_{1.92}/Co₃O₄ sample showed a higher catalytic activity for toluene and *o*-xylene oxidation (the temperature required for achieving 90% conversion of toluene and *o*-xylene was 180 and 187 °C, respectively) than the supported Au or Pd catalyst at a space velocity (SV) of 40000 mL (g⁻¹ h⁻¹). The authors assigned the good catalytic activity of 0.96AuPd_{1.92}/Co₃O₄ to the high concentration of adsorbed oxygen species and strong interaction between Au–Pd nanoparticles (NPs) and Co₃O₄. Xie et al. [13] synthesized a series of the supported Au–Pd catalysts and found that these porous transition-metal oxide-supported Au–Pd NPs showed high activity and good (hydro)thermal stability for toluene or methane combustion. Guo et al. [14] observed better performance for methanol combustion of the TiO₂-supported Pd–Pt NPs than the supported Pd NPs, a result due to a more amount of adsorbed oxygen species on the former than on the latter. Xie et al. [15] pointed out that the three-dimensionally ordered macroporous (3DOM) Co₃O₄-supported Au–Pd–xCoO catalysts performed well in CH₄ combustion.

The choice of a transition-metal oxide support is important in formulating an effective catalyst because it could provide oxygen vacancies that would be favorable for the adsorption and activation of oxygen and/or VOCs molecules [16,17]. Transition-metal oxides were widely used in catalytic oxidation of VOCs because of their good redox ability [18–21]. Among transition-metal oxides, cobalt oxide was used as support for the removal of VOCs and methane [22–24]. In the previous studies, mesoporous cobalt oxides with high surface areas and ordered pore structures showed better catalytic performance than their nonporous counterparts. For example, Wu et al. [25] reported that 2.94Au_{0.5}Pd/meso-Co₃O₄ performed better than 2.90Au_{0.5}Pd/bulk-Co₃O₄ for methane combustion, which was associated with its porous structure, high adsorbed oxygen species concentration, good low-temperature reducibility, and strong interaction between Au–Pd alloy NPs and meso-Co₃O₄. Liu et al. [26] observed excellent performance for benzene, toluene, and *o*-xylene oxidation of the 6.5Au/meso-Co₃O₄ sample with high surface areas.

Previously, our group prepared a series of mesoporous transition-metal oxides (e.g., meso-Co₃O₄ [25,26], meso-MnO_x [27,28], and meso-CrO_x [29,30]) via the KIT-6-templating route, and found that most of these porous materials exhibited good performance for VOC combustion. Although a number of bi-metal alloy catalysts were reported in the literature, there have been no works on the ternary metal alloy catalysts used for VOC combustion. In the present work, we choose Pd as the major active component, add cheaper noble metals (e.g., Ag and Au) to formulate the ternary metal (Ag–Au–Pd) alloy NPs, load them on the surface of meso-Co₃O₄, and investigate catalytic

properties of the as-obtained materials for the combustion of methanol. It is found that the 0.68 wt% Ag_{0.75}Au_{1.14}Pd/meso-Co₃O₄ sample showed the best catalytic activity for the addressed reaction.

2. Experimental

2.1. Synthesis of meso-Co₃O₄

Three-dimensionally mesoporous silica (KIT-6) was synthesized according to the procedures described by Kleitz et al. [31]. We use KIT-6 as the hard template and manganese nitrate as the metal source to fabricate the three-dimensionally ordered mesoporous Co₃O₄ (meso-Co₃O₄). In a typical synthesis, 1.0 g of Co(NO₃)₂·6H₂O was dissolved in 10 mL of ethanol, and then 0.5 g of KIT-6 was added to the Co-containing ethanol solution. The mixture was stirred at 65 °C until the solution was dried. The above mixture was placed in a crucible and calcined in a muffle furnace at a ramp of 1 °C/min from room temperature (RT) to 600 °C and kept at this temperature for 6 h. The obtained powders were leached twice with a hot NaOH aqueous solution (2.0 mol/L), followed by washing with deionized water and ethanol two times and drying at 60 °C for 24 h, thus obtaining the meso-Co₃O₄ support.

2.2. Preparation of meso-Co₃O₄-supported noble metal catalysts

The meso-Co₃O₄-supported Ag_xAu_yPd (Ag/Au/Pd molar ratio = *x* : *y* : 1), Ag, Au, and Pd samples were prepared using the polyvinyl alcohol (PVA)-protected sodium borohydride reduction strategy [28]. The typical preparation procedure is as follows. 2.25 mL of PVA (MW = 10000 g/mol) was added to (i) a mixture of 0.79, 0.34 or 0.40 mL of AgNO₃ aqueous solution (14.7 mmol/L), 0.56, 0.96 or 0.56 mL of HAuCl₄ aqueous solution (10.3 mmol/mL), and 0.21, 0.18 or 0.41 mL of PdCl₂ aqueous solution (28.0 mmol/mL) with the metal/PVA mass ratio = 1.0 : 1.5 and the theoretical Ag:Au:Pd molar ratio was 2:1:1, 1:2:1, and 1:1:2, respectively, or (ii) 0.40 mL of AgNO₃ aqueous solution (14.7 mmol/L), or (iii) 0.56 mL of HAuCl₄ aqueous solution (10.3 mmol/mL), or (iv) 0.41 mL of PdCl₂ aqueous solution (28.0 mmol/mL) at RT under vigorous stirring for 15 min. After rapidly injecting the NaBH₄ aqueous solution (0.1 mol/L, and metal/NaBH₄ molar ratio = 1.0:5.0), a dark-brown sol was generated. 0.3 g of the meso-Co₃O₄ support (the nominal Ag_xAu_yPd loading in each of the supported samples was 1.00 wt%; and the nominal Ag, Au, and Pd loadings in the supported single noble metal samples were 0.42, 0.38, and 0.35 wt%, respectively) was added to the above dark-brown sol under stirring until complete adsorption (the solution was totally decolorized) was achieved. The obtained mixture was filtered, washed with deionized water, dried at 80 °C for 12 h, and calcined at a ramp rate of 1 °C/min from RT to 500 °C and maintained this temperature for 2 h. According to the results of the inductively coupled plasma-atomic emission spectroscopic (ICP-AES) characterization, the 0.68 wt% Ag_{0.75}Au_{1.14}Pd/meso-Co₃O₄, 0.84 wt% Ag_{0.54}Au_{2.29}Pd/meso-Co₃O₄, 0.93 wt% Ag_{0.51}Au_{0.65}Pd/meso-Co₃O₄, 0.28 wt%

Ag/meso-Co₃O₄, 0.35 wt% Au/meso-Co₃O₄, and 0.33 wt% Pd/meso-Co₃O₄ samples were obtained and denoted as 0.68Ag_{0.75}Au_{1.14}Pd/meso-Co₃O₄, 0.84Ag_{0.54}Au_{2.29}Pd/meso-Co₃O₄, 0.93Ag_{0.51}Au_{0.65}Pd/meso-Co₃O₄, 0.28Ag/meso-Co₃O₄, 0.35Au/meso-Co₃O₄, and 0.33Pd/meso-Co₃O₄, respectively.

2.3. Catalyst characterization

The ICP-AES technique was used to detect the actual metal contents of Ag, Au, and Pd in the samples on a Thermo Electron IRIS Intrepid ER/S spectrometer. Before analysis, the sample was dissolved in a mixture of concentrated HCl and HNO₃ with a volumetric ratio of 3:1. X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Advance diffractometer using the Cu K α radiation and nickel filter ($\lambda = 0.15406$ nm). The transmission electron microscopic (TEM) images were obtained on a JEOL JEM-2010 instrument. High angle annular dark field and scanning transmission electron microscopic (HAADF-STEM) techniques were used to record the HAADF-STEM images and EDX element mapping of the typical sample on the equipment FEI G2 80-200/Chemi-STEM Cs-corrected TEM with a probe corrector operated at accelerating voltage 200 kV. Before measurements, a small amount of the sample was ultrasonicated in ethanol for 15 min, and the resulting slurry was then deposited on the copper-coated grids. BET (Brunauer-Emmett-Teller) surface areas and pore-size distributions of the samples were measured via N₂ adsorption at -196 °C on a Micromeritics ASAP 2020 analyzer, with the samples being degassed at 250 °C for 2.5 h under vacuum before measurement.

X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB 250 Xi) was used to determine the binding energies (BEs) of Co 2p, O 1s, Ag 3d, Au 4f, Pd 3d, and C 1s of surface species using Al K α ($h\nu = 1486.6$ eV) as excitation source. In order to remove the adsorbed water and carbonate species on the surface, the samples were pretreated in O₂ (flow rate = 20 mL/min) at 450 °C for 1 h and then cooled to RT, followed by transferring the pretreated samples into the spectrometer in a transparent Glove Bag (Instruments for Research and Industry, USA) filled with helium. The pretreated samples were degassed in the preparation chamber (10^{-5} Torr) for 0.5 h and then introduced into the analysis chamber (3×10^{-9} Torr) for XPS spectrum recording. The C 1s signal at BE = 284.6 eV was taken as reference for BE calibration.

Hydrogen temperature-programmed reduction (H₂-TPR) experiments were carried out on a chemical adsorption analyzer (Autochem II 2920, Micromeritics). Before TPR measurement, ca. 0.03 g of the sample (40–60 mesh) was loaded to a quartz fixed-bed U-shaped microreactor (i.d. = 4 mm) and pretreated in an air flow of 30 mL/min at 250 °C for 1 h. After being cooled at the same atmosphere to RT, the pretreated sample was exposed to a flow (40 mL/min) of 10% H₂–90% Ar (v/v) mixture and heated from RT to 450 °C at a ramp rate of 10 °C/min. The alteration in H₂ concentration of the effluent was monitored online by the chemical adsorption analyzer. The reduction peak was calibrated against that of the complete reduction of a known standard powdered CuO (Aldrich,

99.995%).

2.4. Catalytic activity evaluation

Catalytic activities of the samples were evaluated in a continuous flow fixed-bed quartz microreactor (i.d. = 4.0 mm). 25 mg of the sample (40–60 mesh) was diluted with 0.15 g of quartz sands (40–60 mesh) to minimize the effect of hot spots. A thermocouple was placed in the middle of the catalyst bed, and methanol conversion was measured after 1 h of the reaction that reached a steady state. Before the test, each sample was treated in an oxygen flow of 20 mL/min at 250 °C for 1 h. After being cooled to a given temperature, the reactant gas mixture was passed through the catalyst bed. The total flow rate of reactant gas mixture (0.1 vol% methanol + O₂ + N₂ (balance)) was 33.4 mL/min, giving a methanol/O₂ molar ratio of 1/200 and a space velocity (SV) of ca. 80000 mL (g⁻¹ h⁻¹). The 0.1 vol% methanol was generated by passing a N₂ flow through a pure methanol-containing bottle that was chilled in an ice-water isothermal bath (0 °C). In the case of water vapor introduction, 3.0 vol% H₂O was introduced by passing the feed stream through a water saturator at 33 °C. In the case of CO₂ addition, 5.0 vol% CO₂ was introduced from a CO₂ cylinder with N₂ as the balanced gas. Reactants and products were analyzed online on a gas chromatograph (GC-2010, Shimadzu) equipped with a flame ionization detector (FID), using a stabilwax@-DA column (30 m in length) for methanol separation. Catalytic activities of the samples were evaluated using the temperatures ($T_{50\%}$ and $T_{90\%}$) required for achieving methanol conversions of 50% and 90%, respectively. Methanol conversion was defined as $(C_{\text{inlet}} - C_{\text{outlet}})/C_{\text{inlet}} \times 100\%$, where C_{inlet} and C_{outlet} are toluene concentrations of the inlet and outlet feed stream, respectively. Only CO₂ was detected in the outlet. The balance of carbon throughout the investigation was estimated to be 98.5% $\pm$ 1.5%. Reaction rate per gram of noble metal was calculated according to the following formula: $r = C_{R,\text{in}} \times X/m_{\text{noble metal}}$, where $C_{R,\text{in}}$ (mol/s) is the initial reactant concentration, X is the methanol conversion rate, and $m_{\text{noble metal}}$ (g) is the mass of the catalyst.

3. Results and discussion

3.1. Crystal phase composition, surface morphology, pore structure, and surface area

Fig. 1 shows the wide-angle XRD patterns of the as-prepared samples. All of the diffraction peaks can be well indexed, as indicated in Fig. 1g. By referring to the XRD pattern (JCPDS PDF# 42-1467) of the standard Co₃O₄ sample, one can realize that the Co₃O₄ support was cubic in crystal structure [32,33], and the appearance of a signal at $2\theta \approx 1^\circ$ in the small-angle XRD pattern (not shown here) suggests generation of an ordered mesoporous structure in the Co₃O₄ support, which was synthesized using the same procedures described in our previous works [15,26]. There were no apparent differences in XRD patterns of the supported noble metal samples, indicating that the loading of noble metal NPs did not change the structure of the

Fig. 1. Wide-angle XRD patterns of (a) meso- Co_3O_4 , (b) $0.28\text{Ag}/\text{meso-}\text{Co}_3\text{O}_4$, (c) $0.35\text{Au}/\text{meso-}\text{Co}_3\text{O}_4$, (d) $0.33\text{Pd}/\text{meso-}\text{Co}_3\text{O}_4$, (e) $0.68\text{Ag}_{0.75}\text{Au}_{1.14}\text{Pd}/\text{meso-}\text{Co}_3\text{O}_4$, (f) $0.84\text{Ag}_{0.54}\text{Au}_{2.29}\text{Pd}/\text{meso-}\text{Co}_3\text{O}_4$, and (g) $0.93\text{Ag}_{0.51}\text{Au}_{0.65}\text{Pd}/\text{meso-}\text{Co}_3\text{O}_4$.

support and the noble metal NPs were highly dispersed on the surface of meso- Co_3O_4 .

TEM images shown in Fig. 2 demonstrate that a 3D ordered mesoporous structure was formed in the samples, and the mesopore diameter of meso- Co_3O_4 was ca. 6 nm. Ag, Au, Pd, and $\text{Ag}_x\text{Au}_y\text{Pd}$ NPs were uniformly dispersed on the surface of meso- Co_3O_4 . The HAADF-STEM images of the $0.68\text{Ag}_{0.75}\text{Au}_{1.14}\text{Pd}/$

Fig. 3. HAADF-STEM and elemental scanning images of the $0.68\text{Ag}_{0.75}\text{Au}_{1.14}\text{Pd}/\text{meso-}\text{Co}_3\text{O}_4$ sample.

meso- Co_3O_4 sample is shown in Fig. 3. It can be obviously seen that the NPs in the selected region were composed of Ag, Au, and Pd, indicating formation of the Ag-Au-Pd alloy in $\text{Ag}_{0.75}\text{Au}_{1.14}\text{Pd}$ NPs. After statistically analyzing 100 noble metal NPs in the TEM images, we measured their average sizes and the results are shown in Fig. 4. As summarized in Table 1, the average sizes of Ag, Au, and Pd NPs were 4.1, 4.5, and 2.8 nm, respectively, while those of $\text{Ag}_x\text{Au}_y\text{Pd}$ NPs were 2.9–3.0 nm (Fig. 4).

N_2 adsorption-desorption isotherms and pore-size distributions of the samples are shown in Fig. 5A and B, respectively. All of the samples exhibited a type IV isotherm with a H1 hys-

Fig. 2. TEM images of (a, b) $0.28\text{Ag}/\text{meso-}\text{Co}_3\text{O}_4$, (c, d) $0.35\text{Au}/\text{meso-}\text{Co}_3\text{O}_4$, (e, f) $0.33\text{Pd}/\text{meso-}\text{Co}_3\text{O}_4$, (g, h) $0.68\text{Ag}_{0.75}\text{Au}_{1.14}\text{Pd}/\text{meso-}\text{Co}_3\text{O}_4$, (i, j) $0.84\text{Ag}_{0.54}\text{Au}_{2.29}\text{Pd}/\text{meso-}\text{Co}_3\text{O}_4$, and (k, l) $0.93\text{Ag}_{0.51}\text{Au}_{0.65}\text{Pd}/\text{meso-}\text{Co}_3\text{O}_4$.

Fig. 4. Metal particle size distributions of (a) 0.28Ag/meso-Co₃O₄, (b) 0.35Au/meso-Co₃O₄, (c) 0.33Pd/meso-Co₃O₄, (d) 0.68Ag_{0.75}Au_{1.14}Pd/meso-Co₃O₄, (e) 0.84Ag_{0.54}Au_{2.29}Pd/meso-Co₃O₄, and (f) 0.93Ag_{0.51}Au_{0.65}Pd/meso-Co₃O₄.

Table 1

BET surface areas, average pore diameters, pore volumes, average noble metal particle sizes, actual noble metal molar ratios, and actual noble metal loadings of the as-obtained samples.

Sample	Surface area (m ² /g)	Average pore diameter (nm)	Pore volume (cm ³ /g)	Average noble metal particle size ^a (nm)	Actual Ag: Au: Pd molar ratio ^b	Actual noble metal loading ^b (wt%)	Ag	Au	Pd	Total
meso-Co ₃ O ₄	125	6.1	0.14	—	—	—	—	—	—	—
0.28Ag/meso-Co ₃ O ₄	119	6.0	0.15	4.1	—	0.28	—	—	—	0.28
0.35Au/meso-Co ₃ O ₄	120	5.8	0.16	4.5	—	—	0.35	—	—	0.35
0.33Pd/meso-Co ₃ O ₄	115	5.8	0.16	2.8	—	—	—	0.33	—	0.33
0.68Ag _{0.75} Au _{1.14} Pd/meso-Co ₃ O ₄	120	5.9	0.16	2.9	0.75:1.14:1.00	0.13	0.37	0.18	0.68	0.68
0.84Ag _{0.54} Au _{2.29} Pd/meso-Co ₃ O ₄	119	5.8	0.16	2.9	0.54:2.29:1.00	0.08	0.62	0.14	0.84	0.84
0.93Ag _{0.51} Au _{0.65} Pd/meso-Co ₃ O ₄	120	5.7	0.16	3.0	0.51:0.65:1.00	0.18	0.41	0.34	0.93	0.93

^a Determined according to the TEM images of the samples.

^b Determined by the ICP-AES technique.

teresis loop in the relative pressure (p/p_0) range of 0.4–1.0, demonstrating the generation of ordered mesopores. There was a peak in the pore-size range of 5.7–6.0 nm of each sample (Fig. 5B), further confirming the presence of mesopores in these samples. The above results were in good accordance with those of the small-angle XRD and TEM investigations. Surface areas and pore volumes of the samples are summarized in Table 1. The surface area, average pore size, and pore volume of meso-Co₃O₄ were 125 m²/g, 6.1 nm, and 0.14 cm³/g, respectively. After loading noble metal NPs on the support, however, there were no significant decreases in surface area of the supported noble metal samples. The supported noble metal samples possessed a surface area of 115–120 m²/g, an average pore size of 5.7–6.0 nm, and a pore volume of 0.15–0.16 cm³/g (Table 1).

3.2. Surface element composition, metal oxidation state, and adsorbed oxygen species

XPS technique was applied to investigate the surface element compositions, metal oxidation states, and adsorbed oxygen species of the samples. Fig. 6 shows the Co 2p_{3/2}, O 1s, Ag 3d_{5/2}, Au 4f, and Pd 3d XPS spectra of the samples. By using the curve-fitting method, we can decompose the Co 2p_{3/2} into three components (Fig. 6A): the ones at binding energy (BE) = 779.8 and 781.5 eV were assigned to the surface Co³⁺ and Co²⁺ species, respectively, whereas the one at BE = 788.9 eV was attributed to the satellite signal of the surface Co²⁺ species [34,35]. The asymmetrical O 1s XPS signals could be decomposed into three components at BE = 529.9, 531.3, and 532.7

Fig. 5. (A) N_2 adsorption-desorption isotherms and (B) pore-size distributions of (a) meso- Co_3O_4 , (b) 0.28Ag/meso- Co_3O_4 , (c) 0.35Au/meso- Co_3O_4 , (d) 0.33Pd/meso- Co_3O_4 , (e) 0.68Ag_{0.75}Au_{1.14}Pd/meso- Co_3O_4 , (f) 0.84Ag_{0.54}Au_{2.29}Pd/meso- Co_3O_4 , and (g) 0.93Ag_{0.51}Au_{0.65}Pd/meso- Co_3O_4 .

eV (Fig. 6B), ascribable to the surface lattice oxygen (O_{latt}), adsorbed oxygen (O_{ads} , e.g., O_2^- , O_2^{2-} or O^-), and adsorbed molecular water or carbonate species [36], respectively. It is well known that there is a close link between the ability to activate oxygen and the activity of a catalyst. The electrophilic O_2^- , O_2^{2-} or O^- species can play an important role in the oxidation of organics. The supported Ag_xAu_yPd NPs possessed much higher amounts of the O_{ads} species than the supported Ag, Au or Pd NPs, making the former outperform the latter for methanol combustion, as confirmed by their activity data. The broad and asymmetrical Ag $3d_{5/2}$ XPS signal of each sample could be deconvoluted into two components at BE = 367.5 and 368.0 eV, which was ascribed to the surface Ag⁺ and Ag⁰ species [37,38], respectively. The Au XPS signal of each sample could be decomposed into four components (Fig. 6D): the ones at BE = 84.0 and 87.7 eV were attributed to the surface Au⁰ species, whereas the ones at BE = 85.1 and 88.7 eV were assigned to the surface Au^{δ+} species [39]. As shown in Fig. 6E, the Pd $3d$ XPS signal was decomposed into two sets of components: the ones at BE = 335.5 and 340.7 eV were assignable to the surface Pd⁰ species, while the ones at BE = 337.2 and 342.4 eV were attributable to the surface Pd²⁺ species [40,41]. A higher Pd²⁺/Pd⁰ molar ratio could also favor the improvement in catalytic activity because Pd²⁺ was the active site for activation of VOCs. The surface element compositions of the samples are summarized in Table 2. After loading Ag_xAu_yPd NPs on meso- Co_3O_4 , the surface Co^{3+}/Co^{2+} molar ratio decreased from 0.80–0.90 to 0.60–0.69 (Table 2), indicating that the surface Co^{2+} concentration increased. Such a decrease in Co^{3+}/Co^{2+} molar ratio as well as formation of the Au^{δ+}, Ag⁺, and Pd²⁺ species was due to the enhanced strong interaction between noble metal NPs and support. Obviously, the 0.68Ag_{0.75}Au_{1.14}Pd/meso- Co_3O_4 sample possessed the lowest surface Co^{3+}/Co^{2+} molar ratio. In other words, there was the highest oxygen vacancy concentration on

the surface of 0.68Ag_{0.75}Au_{1.14}Pd/meso- Co_3O_4 . A more amount of oxygen vacancies can give rise to a more amount of the O_{ads} species, consequently resulting in a better performance of a catalyst. Therefore, it is understandable that the 0.68Ag_{0.75}Au_{1.14}Pd/meso- Co_3O_4 sample showed the best activity for the oxidation of methanol.

3.3. Reducibility

H_2 -TPR profiles of the samples are shown in Fig. 7A. According to the literature, the two reduction peaks at 300 and 320–410 °C of the Co_3O_4 sample were ascribable to reduction of Co^{3+} to Co^{2+} and of Co^{2+} to Co^0 [42,43], respectively. After loading Ag and Au, the newly appeared peaks at 200 and 265 °C were attributable to the reduction of these noble metal oxides. When Pd or Ag_xAu_yPd was loaded on the surface of meso- Co_3O_4 , the reduction peaks were significantly shifted to low temperatures (the first peak at 115 °C was mainly due to reduction of PdO_x, and the reduction of Co^{3+} and Co^{2+} was shifted to a lower temperature, which indicates the presence of a strong interaction between noble metal alloy NPs and support). Such a phenomenon was a result due to reduction of meso- Co_3O_4 promoted by the hydrogen chemically adsorbed on Pd or Ag_xAu_yPd NPs. The results demonstrate that loading of Pd or Ag_xAu_yPd NPs considerably improved the low-temperature reducibility of the sample. By quantitatively analyzing the reduction peaks in the H_2 -TPR profiles, one can obtain the H_2 consumption of the samples, as summarized in Table 2. The H_2 consumptions of the samples were in the range of 19.6–21.0 mmol/g_{cat} (slightly higher than the theoretical H_2 consumption of Co_3O_4), which was due to the reduction of the oxidized noble metal NPs and the removal of the adsorbed oxygen species.

The initial H_2 consumption rate was calculated according to the H_2 consumption per gram of catalyst per second, which

Fig. 6. (A) Co 2p_{3/2}, (B) O 1s, (C) Ag 3d_{5/2}, (D) Au 4f, and (E) Pd 3d XPS spectra of (a) 0.28Ag/meso-Co₃O₄, (b) 0.35Au/meso-Co₃O₄, (c) 0.33Pd/meso-Co₃O₄, (d) 0.68Ag_{0.75}Au_{1.14}Pd/meso-Co₃O₄, (e) 0.84Ag_{0.54}Au_{2.29}Pd/meso-Co₃O₄, and (f) 0.93Ag_{0.51}Au_{0.65}Pd/meso-Co₃O₄.

Table 2

Surface element compositions, H₂ consumption, catalytic activities, and TOF_{noble metal} at SV = 80000 mL g⁻¹ h⁻¹ of the samples.

Sample	Surface element composition a (mol/mol)					H ₂ consumption ^b (mmol/g _{cat})	Catalytic activity		TOF _{noble metal} at 100 °C (10 ⁻³ s ⁻¹)
	Co ³⁺ /Co ²⁺	Ag ⁺ /Ag ⁰	Au ³⁺ /Au ⁰	Pd ²⁺ /Pd ⁰	O _{ads} /O _{latt}		T _{50%} (°C)	T _{90%} (°C)	
0.28Ag/meso-Co ₃ O ₄	0.90	0.32	—	—	0.33	19.9	148	176	2.8
0.35Au/meso-Co ₃ O ₄	0.88	—	0.11	—	0.34	21.0	144	174	4.3
0.33Pd/meso-Co ₃ O ₄	0.80	—	—	0.42	0.36	19.6	124	162	5.1
0.68Ag _{0.75} Au _{1.14} Pd/meso-Co ₃ O ₄	0.60	0.87	0.17	0.55	0.63	20.9	100	112	13.0
0.84Ag _{0.54} Au _{2.29} Pd/meso-Co ₃ O ₄	0.69	0.77	0.17	0.56	0.44	19.8	109	140	6.8
0.93Ag _{0.51} Au _{0.65} Pd/meso-Co ₃ O ₄	0.63	0.44	0.13	0.42	0.60	20.1	105	126	5.5

^a Calculated by quantitatively analyzing the peaks in XPS spectra of the samples.

^b Calculated by quantitatively analyzing the peaks in H₂-TPR profiles of the samples.

corresponded to the initial 25% of the first reduction peak where no phase transformation of the sample occurred [44,45]. The results are shown in Fig. 7B. The initial H₂ consumption rate increased in the sequence of 0.28Ag/meso-Co₃O₄ < 0.35Au/meso-Co₃O₄ < 0.33Pd/meso-Co₃O₄ < 0.84Ag_{0.54}Au_{2.29}Pd/meso-Co₃O₄ < 0.93Ag_{0.51}Au_{0.65}Pd/meso-Co₃O₄ < 0.68Ag_{0.75}Au_{1.14}Pd/meso-Co₃O₄. That is to say, the 0.68Ag_{0.75}Au_{1.14}Pd/meso-Co₃O₄ sample exhibited the best low-temperature reducibility. The trend in low-temperature reducibility was in agreement with the order in catalytic activi-

ty of the samples (shown below).

3.4. Catalytic performance

No significant methanol conversions (< 2%) at temperature < 220 °C and SV = 80000 mL g⁻¹ h⁻¹ were detected in the blank experiment (only quartz sands were loaded in the microreactor), indicating that no considerable gas-phase reaction existed in the catalytic system. Fig. 8A shows the catalytic activities of the as-prepared samples at SV = 80000 mL g⁻¹ h⁻¹. Obviously,

Fig. 7. (A) H₂-TPR profiles and (B) initial H₂ consumption rate of (a) 0.28Ag/meso-Co₃O₄, (b) 0.35Au/meso-Co₃O₄, (c) 0.33Pd/meso-Co₃O₄, (d) 0.68Ag_{0.75}Au_{1.14}Pd/meso-Co₃O₄, (e) 0.84Ag_{0.54}Au_{2.29}Pd/meso-Co₃O₄, and (f) 0.93Ag_{0.51}Au_{0.65}Pd/meso-Co₃O₄.

the supported Ag_xAu_yPd samples outperformed the supported Ag, Au or Pd sample. Among the supported Ag_xAu_yPd samples, catalytic activity decreased in the order of 0.68Ag_{0.75}Au_{1.14}Pd/meso-Co₃O₄ > 0.93Ag_{0.51}Au_{0.65}Pd/meso-Co₃O₄ > 0.84Ag_{0.54}Au_{2.29}Pd/meso-Co₃O₄, with the 0.68Ag_{0.75}Au_{1.14}Pd/meso-Co₃O₄ sample exhibiting the highest activity ($T_{50\%} = 100$ °C and $T_{90\%} = 112$ °C at SV = 80000 mL g⁻¹ h⁻¹). Fig. 8B shows the methanol reaction rate normalized per gram of noble metal versus temperature of the samples. It can be seen that the 0.28Ag/meso-Co₃O₄ sample almost showed the same reaction rate as the 0.35Au/meso-Co₃O₄ sample, while the supported Pd sample performed better than the supported Ag or Au sample. The reaction rate decreased in the order of 0.68Ag_{0.75}Au_{1.14}Pd/meso-Co₃O₄ > 0.33Pd/meso-Co₃O₄ > 0.93Ag_{0.51}Au_{0.65}Pd/meso-Co₃O₄ ≈ 0.84Ag_{0.54}Au_{2.29}Pd/meso-Co₃O₄ > 0.35Au/meso-Co₃O₄ ≈ 0.28Ag/meso-Co₃O₄, with the 0.68Ag_{0.75}Au_{1.14}Pd/meso-Co₃O₄ sample possessing the highest catalytic efficiency. The turnover frequencies (TOF_{noble metal}) normalized per gram of noble metal at 100 °C ($\times 10^{-3}$ s⁻¹) were calculated and summarized in Table 2. The 0.68Ag_{0.75}Au_{1.14}Pd/meso-Co₃O₄ sample possessed the highest TOF_{noble metal} as well as the highest methanol conversion and reaction rate, which might be a result due to the good dispersion of Ag_{0.75}Au_{1.14}Pd alloy NPs, high adsorbed oxygen species concentration, good low-temperature reducibility, and strong interaction between Ag_{0.75}Au_{1.14}Pd alloy NPs and meso-Co₃O₄. The above results demonstrate that the alloying of Pd with proper amounts of Ag and Au favored the enhancement in methanol combustion activity of the sample.

There have been several works on the oxidation of methanol over various catalysts in the literature. Our 0.68Ag_{0.75}Au_{1.14}Pd/meso-Co₃O₄ sample showed a methanol reaction rate at 100 °C of 0.99 μmol g_{cat}⁻¹ s⁻¹, which was higher

than that (0.01 μmol g_{cat}⁻¹ s⁻¹) over meso-Cr₂O₃ [30], that (0.03 μmol g_{cat}⁻¹ s⁻¹) over wormhole-like Fe₂O₃ [46], that (0.11 μmol g_{cat}⁻¹ s⁻¹) over meso-Co₃O₄ [47], that (0.60 μmol g_{cat}⁻¹ s⁻¹) over 12 wt% MnO_x/3DOM LaMnO₃ [48], that (0.45 μmol g_{cat}⁻¹ s⁻¹) over 2 wt% Ag/CeO₂ [49], and that (0.88 μmol g_{cat}⁻¹ s⁻¹) over 0.1 wt% Pd/5.0 wt% Ag/35CZA [50], but lower than that (3.50 μmol g_{cat}⁻¹ s⁻¹) over 0.8% Pd-Pt/CeO₂-Al₂O₃-TiO₂ [14].

Considering a weak mobility of lattice oxygen in meso-Co₃O₄ at low temperatures, methanol combustion over Ag_xAu_yPd/meso-Co₃O₄ would hardly follow the Mars van Krevelen-type mechanism under the present reaction conditions. The interface mechanism could work well for methanol combustion over the reducible oxide-supported noble metal catalysts. Gas-phase oxygen was adsorbed on the surface oxygen vacancies of meso-Co₃O₄ to produce the active oxygen species, and methanol was adsorbed on the noble metal sites of the catalysts to form methoxy species that were easily oxidized to the formate species by the active oxygen species [49]; then, the generated formate species decomposed to CO and hydroxyl species; and finally, the formed CO was completely oxidized to CO₂.

It is well known that catalytic activity is intimately associated with the transition-metal oxidation state, O_{ads} species concentration, and reducibility of a sample. The O_{ads}/O_{latt} molar ratio versus surface Co³⁺/Co²⁺ molar ratio and methanol reaction rate at 100 °C versus O_{ads}/O_{latt} molar ratio or initial H₂ consumption rate of the samples are shown in Fig. 9. It can be observed that (i) the O_{ads}/O_{latt} molar ratio increased with a drop in surface Co³⁺/Co²⁺ molar ratio (i.e., an increase in surface oxygen vacancy density that was induced by the strong interaction between noble metal NPs and meso-Co₃O₄) (Fig. 9A), (ii) methanol reaction rate increased with increasing the O_{ads}/O_{latt} molar ratio (Fig. 9B), and (iii) methanol reaction rate

Fig. 8. (A) Methanol conversion and (B) reaction rate normalized per gram of noble metal versus temperature over (a) 0.28Ag/meso-Co₃O₄, (b) 0.35Au/meso-Co₃O₄, (c) 0.33Pd/meso-Co₃O₄, (d) 0.68Ag_{0.75}Au_{1.14}Pd/meso-Co₃O₄, (e) 0.84Ag_{0.54}Au_{2.29}Pd/meso-Co₃O₄, and (f) 0.93Ag_{0.51}Au_{0.65}Pd/meso-Co₃O₄.

Fig. 9. (A) O_{ads}/O_{latt} molar ratio versus surface Co^{3+}/Co^{2+} molar ratio, (B) methanol reaction rate versus O_{ads}/O_{latt} molar ratio, and (C) methanol reaction rate versus initial H₂ consumption rate of the samples.

increased with an increase in initial H₂ consumption rate (i.e., low-temperature reducibility) (Fig. 9C). Among all of the samples, 0.68Ag_{0.75}Au_{1.14}Pd/meso-Co₃O₄ possessed the highest O_{ads} species concentration (the lowest Co^{3+}/Co^{2+} molar ratio gave rise to the highest oxygen vacancy density) and the best low-temperature reducibility, hence showing the best catalytic performance for methanol combustion.

3.5. Effect of water and carbon dioxide on activity

Because water vapor exerted a negative effect on catalytic activity for the oxidation of VOCs [51], it is necessary to examine the effect of water vapor on catalytic activity of the typical sample. By introducing 3.0 vol% water vapor to the reaction system, we measured methanol conversions at 110 °C and SV = 80000 mL g⁻¹ h⁻¹ over the 0.68Ag_{0.75}Au_{1.14}Pd/meso-Co₃O₄ sample, as shown in Fig. 10A. It is well known that water is easily

adsorbed on the surface of noble metal (especially Pd) NPs. Obviously, methanol conversion dropped by ca. 6% after addition of 3.0 vol% water vapor. When water vapor was cut off, methanol conversion was restored to its original value in the absence of water vapor, indicating that the partial deactivation induced by water vapor addition was reversible. Such a partial deactivation was due to the competitive adsorption of H₂O and methanol as well as O₂, leading to a decrease in catalytic activity [52,53].

As one of the products of methanol combustion, CO₂ might influence the activity of a catalyst. To examine the effect of CO₂ on activity, we conducted methanol combustion at 110 °C and SV = 80000 mL g⁻¹ h⁻¹ over 0.68Ag_{0.75}Au_{1.14}Pd/meso-Co₃O₄ in the presence of 5.0 vol% CO₂, and the results are shown in Fig. 10B. It is apparent that methanol conversion decreased by ca. 7% after 15 h of on-stream reaction. When CO₂ was cut off, methanol conversion was recovered to its original value in the

Fig. 10. Effects of (A) 3.0 vol% H₂O and (B) 5.0 vol% CO₂ on methanol oxidation over the 0.68Ag_{0.75}Au_{1.14}Pd/meso-Co₃O₄ sample at 110 °C and SV = 80000 mL g⁻¹ h⁻¹.

absence of carbon dioxide. CO₂ molecules were adsorbed on the active sites of the sample to form the CO₃²⁻ or HCO₃⁻ species, thus influencing the activity. After CO₂ was cut off, however, these carbonate species were possibly desorbed from the active sites of the sample, hence recovering the occupied active sites.

4. Conclusions

The cubically crystallized meso-Co₃O₄ and its supported Ag_xAu_yPd, Ag, Au, and Pd catalysts were prepared using the KIT-6-templating and PVA-protected NaBH₄ reduction methods, respectively. The as-obtained materials displayed a three-dimensionally ordered mesoporous structure and a high surface area (115–125 m²/g), and the noble metal NPs with an average size of 2.8–4.5 nm were highly dispersed on the surface of meso-Co₃O₄. The supported Ag_xAu_yPd samples outperformed the Ag, Au or Pd sample, with the 0.68Ag_{0.75}Au_{1.14}Pd/meso-Co₃O₄ sample showing the highest catalytic activity ($T_{50\%}$ = 100 °C and $T_{90\%}$ = 112 °C at SV = 80000 mL g⁻¹ h⁻¹) for methanol combustion. The partial deactivation due to H₂O or CO₂ addition of the 0.68Ag_{0.75}Au_{1.14}Pd/meso-Co₃O₄ sample was reversible. It is concluded that the good catalytic performance of 0.68Ag_{0.75}Au_{1.14}Pd/meso-Co₃O₄ was related to the highly dispersed Ag_{0.75}Au_{1.14}Pd alloy NPs, high O_{ads} species concentration, good low-temperature reducibility, and strong interaction between Ag_{0.75}Au_{1.14}Pd alloy NPs and meso-Co₃O₄.

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Graphical Abstract

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AgAuPd/meso-Co₃O₄: High-performance catalysts for methanol oxidation

Jun Yang, Yuxi Liu*, Jiguang Deng, Xingtian Zhao, Kunfeng Zhang, Zhuo Han, Hongxing Dai*
Beijing University of Technology

Ag_xAu_yPd/meso-Co₃O₄ catalysts are prepared using the KIT-6-templating and PVA-protected reduction methods. The good catalytic activity of 0.68 wt% Ag_{0.75}Au_{1.14}Pd/meso-Co₃O₄ for methanol combustion is associated with its highly dispersed Ag_{0.75}Au_{1.14}Pd alloy nanoparticles (NPs), high O_{ads} species concentration, good low-temperature reducibility, and strong interaction between noble metal NPs and meso-Co₃O₄.

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AgAuPd/meso-Co₃O₄高效甲醇氧化催化剂

杨 军, 刘雨溪*, 邓积光, 赵星天, 张昆锋, 韩 卓, 戴洪兴#

北京工业大学环境与能源工程学院化学化工系, 绿色催化与分离北京市重点实验室, 区域大气复合污染防治北京市重点实验室, 先进功能材料教育部重点实验室, 催化化学与纳米科学实验室, 北京100124

摘要: 甲醇是重要的化工原料和溶剂, 也是一种典型的挥发性有机物(VOCs), 其排放会对人体和大气环境造成危害。迄今为止, 最有效的消除低浓度VOCs的方法是催化氧化。该方法具有VOCs去除效率高、起燃温度低、设备简单且无二次污染等优点。众所周知, 负载贵金属催化剂对VOCs氧化显示良好的低温活性, 但反应气流中的水分会降低贵金属的催化性能。

研究表明,与单一贵金属催化剂相比,贵金属合金催化剂不仅具有高的催化活性,而且还具有良好的水热稳定性。尽管已有文献报道了二元贵金属合金催化剂对VOCs的催化氧化,然而VOCs在三元贵金属合金上催化氧化的研究则较少。本文采用三维有序介孔结构的二氧化硅(KIT-6)硬模板法和聚乙烯醇保护的硼氢化钠还原法制备了0.68 wt% $\text{Ag}_{0.75}\text{Au}_{1.14}\text{Pd}/\text{meso-Co}_3\text{O}_4$, 0.84 wt% $\text{Ag}_{0.54}\text{Au}_{2.29}\text{Pd}/\text{meso-Co}_3\text{O}_4$ 和0.93 wt% $\text{Ag}_{0.51}\text{Au}_{0.65}\text{Pd}/\text{meso-Co}_3\text{O}_4$ 三元贵金属合金催化剂以及0.28 wt% $\text{Ag}/\text{meso-Co}_3\text{O}_4$, 0.35 wt% $\text{Au}/\text{meso-Co}_3\text{O}_4$ 和0.33 wt% $\text{Pd}/\text{meso-Co}_3\text{O}_4$ 单一贵金属催化剂。利用电感耦合等离子体-原子发射光谱(ICP-AES)、X射线衍射(XRD)、透射电子显微镜(TEM)、高角环形暗场-扫描透射电子显微镜(HAADF-STEM)、X射线光电子能谱(XPS)和氢气-程序升温还原(H_2 -TPR)技术表征了催化剂的物化性质。催化剂的活性评价在固定床石英微型反应器中进行,反应气组成为0.1% 甲醇 + 氧气 + 氮气(平衡气),甲醇/氧气摩尔比为1/200,空速约为80000 $\text{mL g}^{-1} \text{h}^{-1}$,利用气相色谱检测反应物和产物的浓度。

广角度XRD结果表明,meso- Co_3O_4 具有立方晶相结构。XRD谱中未检测到Ag, Au和Pd的衍射峰,系贵金属负载量低且均匀分散在载体表面所致。贵金属粒径为2.8–4.5 nm。小角度XRD和TEM结果表明,meso- Co_3O_4 具有有序介孔结构。从HAADF-STEM照片可以观察到,0.68 wt% $\text{Ag}_{0.75}\text{Au}_{1.14}\text{Pd}/\text{meso-Co}_3\text{O}_4$ 中的贵金属形成了Ag-Au-Pd合金。BET结果显示,所制得催化剂的比表面积为115–120 m^2/g ,孔径为5.7–6.0 nm,孔容为0.15–0.16 cm^3/g 。XPS结果表明,贵金属与载体之间较强的相互作用使0.68 wt% $\text{Ag}_{0.75}\text{Au}_{1.14}\text{Pd}/\text{meso-Co}_3\text{O}_4$ 具有最低的表面 $\text{Co}^{3+}/\text{Co}^{2+}$ 摩尔比,从而使该催化剂表面拥有更多的氧空位,有利于吸附和活化氧气,提高表面吸附氧浓度,从而提高催化活性。0.68 wt% $\text{Ag}_{0.75}\text{Au}_{1.14}\text{Pd}/\text{meso-Co}_3\text{O}_4$ 具有最低的还原温度(即最好的低温还原性),有利于催化活性的提高。因此,高分散的 $\text{Ag}_{0.75}\text{Au}_{1.14}\text{Pd}$ 纳米粒子、高的吸附氧浓度、优良的低温还原性以及载体与 $\text{Ag}_{0.75}\text{Au}_{1.14}\text{Pd}$ 粒子之间强的相互作用是0.68 $\text{Ag}_{0.75}\text{Au}_{1.14}\text{Pd}/\text{meso-Co}_3\text{O}_4$ 具有最高催化活性(当空速为80000 $\text{mL g}^{-1} \text{h}^{-1}$ 时, $T_{50\%} = 100^\circ\text{C}$ 和 $T_{90\%} = 112^\circ\text{C}$)的主要原因。在反应温度为110 $^\circ\text{C}$ 和空速为80000 $\text{mL g}^{-1} \text{h}^{-1}$ 的条件下,向反应体系中分别引入3.0 vol%水蒸气和5.0 vol%二氧化碳,甲醇转化率分别下降6.0%和7.0%;当切断水和二氧化碳后,甲醇转化率均恢复到在水和二氧化碳时的数值。因此,水和二氧化碳对该催化剂的失活是可逆的。换句话说,0.68 wt% $\text{Ag}_{0.75}\text{Au}_{1.14}\text{Pd}/\text{meso-Co}_3\text{O}_4$ 具有优良的水热稳定性和抗二氧化碳中毒能力。

关键词: 挥发性有机物; 介孔四氧化三钴; 负载贵金属催化剂; AgAuPd合金纳米粒子; 甲醇氧化

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*通讯联系人. 电话: (010)67396118; 传真: (010)67391983; 电子信箱: yxliu@bjut.edu.cn

#通讯联系人. 电话: (010)67396118; 传真: (010)67391983; 电子信箱: hxdai@bjut.edu.cn

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