Research Article

Ag-Cu Bimetallic Nanoparticles Prepared by Microemulsion Method as Catalyst for Epoxidation of Styrene

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Ag/Cu bimetallic nanocatalysts supported on reticulate-like γ -alumina were prepared by a microemulsion method using $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ as the reducing agent. The catalysts were activated by calcination followed with hydrogen reduction at 873K, and the properties were confirmed using various characterization techniques. Compared with metal oxides particles, Ag-Cu particles exhibited smaller sizes (<5 nm) after calcination in H_2 at 873K. XPS results indicated that the binding energies changed with the Ag/Cu ratios, suggesting that increasing the copper content gave both metals a greater tendency to lose electrons. Furthermore, Ag-Cu bimetallic nanoparticles supported on γ -alumina showed better catalytic activity on the epoxidation of styrene as compared with the corresponding monometallic silver or copper. The styrene oxide selectivity could reach 76.6% at Ag/Cu molar ratio of 3/1, while the maximum conversion (up to 94.6%) appeared at Ag/Cu molar ratio of 1/1 because of the maximum interaction between silver and copper.

1. Introduction

In recent years, research on silver, copper and gold nanoparticles used as catalysts in CO redox reactions [1–3], NO_x reduction [4, 5] and epoxidation of alkenes [6–9] has made great progress. Because of an altered electronic or surface structure of the metal particles, metal nanoparticle catalysts composed of two (or more) different metal elements may result in improved catalyst quality or properties and hence are of great interest from both technological and scientific views [10]. There have been several reports on the synthesis and assembly of bimetal materials such as Pd-Pt [11], Au-Ag [3], Pt-Co [12], and Ni-Mo [13]. Especially, Agrawal et al. [14] made a series of studies on bimetallic or multimetallic nanoparticle catalysts, for example, Au-Ag, Au-Cu, and Au-Ag-Cu. Alumina-based supports are often used in these catalysts because of their mechanical and chemical resistance under reaction conditions. For instance, an alumina supported silver/copper catalyst has a higher ammonia oxidation

activity than catalysts with pure silver or copper particles [15].

Although the Ag-Cu catalyst system has shown excellent catalytic activity in many oxidation reactions, an attempt about using Ag-Cu as catalyst for oxidation of styrene is rarely reported. Oxidation of styrene may be regarded as a very strategic reaction in industrial applications, because styrene oxide (a main product of oxidation of styrene) is one of the most important fine chemical intermediates for producing perfume, drugs, sweeteners, epoxy resins, and so forth [16]. However, it is difficult to find a catalyst that accelerates both conversion and selectivity for this reaction. To solve this problem, Ag-Cu systems are tested herein to see whether this catalyst could meet the requirements.

In order to better understand the working mechanism of such catalysts, it is essential to prepare model systems with a high degree of control over the particle size of the active material. In the past decade, several methods have been used to produce supported catalysts, but it is difficult

to immobilize the nanoparticles on catalyst supports without large aggregates. Water-in-oil microemulsions are transparent, isotropic, and thermodynamically stable nanosized water droplets that are dispersed in a continuous oil phase and stabilized by surfactant molecules at the water/oil interface [17]. This technique has been used for synthesizing various of nanosized particles, such as Cu [18], Au-Ag [17], KCoFePBA [19], and γ -Al₂O₃ nanoparticles [20]. It is suitable for the preparation of particles, because not only the size but also the shape of the particles can be controlled by altering the water-to-surfactant molar ratio (ω) appropriately. The unique advantages of this method, compared to other techniques for controlled nanoparticle preparation, are that the particles can be formed at atmospheric pressure and at room temperature and that large sample volumes can be obtained relatively easily [21].

In this study, we have investigated the deposition of Ag-Cu bimetallic nanoparticles by the coreduction of Ag⁺ and Cu²⁺ with N₂H₄·H₂O as reductant, prepared in w/o microemulsions, on reticulate-like γ -alumina particles which are obtained through the microemulsion technique by our group [22]. After calcination and reduction at 873 K for one hour by H₂, these materials were characterized by several techniques in order to determine their physicochemical compositions. Finally, the performances of catalysts with different molar ratios of Ag/Cu supported on γ -alumina were tested by epoxidation of styrene under mild conditions.

2. Experimental Section

2.1. Chemicals. The nonionic surfactant Triton X-100 [*p*-tert-C₈H₁₇C₆H₄(OC₂H₄)_{9.5}OH] was obtained from Sigma-Aldrich. Cyclohexane (C₆H₁₂, A.R.) used as oil phase and *n*-butanol [CH₃(CH₂)₂CH₂OH, A.R.] used as the cosurfactant were both purchased from Tianjin Chemical Reagent Limited Company. Silver nitrate (AgNO₃, A.R.) was product from Beijing Beihua Fine Chemical Reagent Co., Ltd., Cupric nitrate [Cu(NO₃)₂·3H₂O, 99.5%, A.R.] was received from the Third Branch of Tianjin Chemical Reagent Liu Chang. Aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O, A.R.) was purchased from Xi'an Chemical Reagent Factory. Ammonia (NH₃·H₂O, 30%, A.R.) was Baiyin LiangYou Chemical Reagent Limited Company products. Styrene (C₈H₈, C.P.) and bromobenzene (C₆H₅Br, A.R.) were bought from Sinopharm Chemical Reagent Limited Company. Hydrazine hydrate (H₂N·NH₂·H₂O, 80.0%, A.R.) was reductant from Tianjin Institute of Fine Chemicals Retrocession. Acetonitrile (CH₃CN, A.R.) used as solvents was received from Tianjin Chemical Reagent Limited Company and tert-butyl hydroperoxide (TBHP)[C₄H₁₀O₂, 70%, C.P.] used as oxidant was bought from Shanghai Sanpu chemical Co., Ltd., Double distilled water was used throughout the experiments.

2.2. Instrumentation. The actual total metal loadings and the Ag/Cu molar ratios of various Ag-Cu/Al₂O₃ samples were determined by the inductively coupled plasma spectrometer on an IRIS ER/S PHEMO instrument. Energy-dispersive X-ray spectroscopy (EDS) (JSM-5600LV, KEVEX) and inductively coupled plasma (ICP) (IRIS ER/S, U.S. PHEMO

company) confirmed the molar ratios of Ag/Cu. Chemical composition information about the samples was obtained by X-ray photoelectron spectroscopy (XPS). The measurement was carried out on a PHI-5702 multifunctional spectrometer using Al K α radiation, and the binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. All the peaks were fitted using the XPSPEAK version 4.0 peak-fitting program. The specific surface areas of the catalysts and the γ -Al₂O₃ support were calculated by applying the BET method to the N₂ adsorption isotherms, measured at liquid nitrogen temperature on a micromeritics ASAP 2010 apparatus. Rigaku D/MAX-2400 XRD with graphite monochromatized Cu K α radiation (λ = 0.15406 nm) was used for recording X-ray diffraction (XRD) pattern operating at 40 kV and 40 mA in the 2 θ range of 10°–90°. Transmission electron microscopy (TEM) was performed by using a Hitachi H-600 at an accelerating voltage of 100 kV to examine the morphology and dimension of the Ag-Cu nanoparticles as well as nanoalumina. Whether the Ag-Cu nanoparticles supported on the alumina or not was shown clearly via this testing technique. The infrared spectroscopy (IR) spectra were recorded on a NEXUS670 FT-IR spectrometer with samples prepared as KBr pellets. The products of reaction were detected by Gas Chromatography (GC) on a CP-3380 instrument.

2.3. Synthesis. Catalysts of Ag-Cu nanoparticles supported on γ -alumina were synthesized by microemulsion technology (Triton X-100/*n*-butanol/cyclohexane/water system) [22]. Briefly, AgNO₃ and Cu(NO₃)₂ microemulsion with different Ag/Cu atomic ratios as well as the hydrazine hydrate microemulsion were obtained with the same component ratio as the Al(NO₃)₃ microemulsion. Ammonia microemulsion was added dropwise into Al(NO₃)₃ microemulsion with a speed at 4–5 s/d accompanied by stirring. After ammonia microemulsion was dropwise up, 40-minute more reaction time was needed. At the fixed temperature of 293 K, various atomic ratios AgNO₃ and Cu(NO₃)₂ microemulsion were added directly, meanwhile, vigorously stirred for one hour. Thereafter, hydrazine hydrate microemulsion was thrown into the mixture at the same speed 4–5 s/d in order to obtain Ag-Cu bimetallic nanoparticles supported on Aluminum hydroxide. After the total mixture was continuously stirred for 2.5 hours at 293 K, the precipitates were centrifuged one time at 12000 rpm for 40 s and then calcined in air at 893 K for 4 hours. Finally, the solids were reduced at 873 K in H₂ (0.15 mL/min) for one hour, subsequently cooled to room temperature under N₂ flow (0.15 mL/min) to obtain the Ag-Cu/Al₂O₃ catalyst. In all cases, the nominal total metal loading was 2 wt%.

2.4. Catalytic Reaction Tests. The activity of the supported Ag-Cu materials was investigated in the epoxidation of styrene. Before the measurement, the catalyst was prereduced in situ in 99% H₂ at 873 K for 1 h. In a typical oxidation test, 0.5 mmol styrene, 1.5 mmol TBHP, and 5 mg catalyst were added to a 25 mL flask, acetonitrile used as solvents, and the temperature maintained at 355 K. The mixture was kept vigorous stirring for another 6 hours and thereafter was

centrifuged in order to remove the catalyst. The main products were styrene epoxide and phenylaldehyde, as verified by GC using bromobenzene as internal standard.

3. Results and Discussion

3.1. Physical Properties of Catalysts. Table 1 lists the BET surface area, pore volume and average pore size of the catalysts with different Ag/Cu molar ratios. All samples display typical Langmuir type-IV isotherm with a clear adsorption-desorption hysteresis loop (Figure 1). The pore sizes are between 16 and 21 nm; The BET surface areas and the pore volume of the catalysts are in the range of 250~330 cm²/g and 1.05~1.67 cm³/g, respectively. Compared with the results reported by Tian [20], the surface areas and the pore volume are higher than pure reticulate-like γ -Al₂O₃ with the values of 209 m²/g and 0.58 cm³/g, which understandably provides plenty of opportunities for molecular collisions when the bimetallic samples used as a catalyst.

In addition, the EDS results show that the measured molar ratios are slightly larger than the nominal ratios, while the results confirmed by ICP are slightly lower than the nominal ratios. The difference may result from that Cu is more highly dispersed in alumina than Ag [15], which may be observed more directly compare Ag/Cu molar ratio of 1/0 to 0/1 from ICP results so that the area with large black particles contains larger amounts of Ag relative to Cu.

3.2. Morphology and Distribution. We used the microemulsion method to prepare the γ -alumina predecessor, then two metal salts microemulsion were added and chemically reduced using the N₂H₄·H₂O microemulsion as reductant. When the N₂H₄·H₂O microemulsion was slowly added to reduce the two metal ions, the colorless solution slowly turned yellow or golden brown during the reduction process, which indicated the formation of metal colloidal nanoclusters. γ -alumina with different morphologies, such as nanofibers, anomalous spherical particles, and reticulate-like nanostructure [20] used as supports, have been investigated. Overall, it is noticed that reticulate-like nanostructure γ -Alumina has a better distribution for silver and copper because of an ordered pore structure. Figure 2(a) shows the TEM images of Ag/Cu bimetallic particles in reticulate-like γ -Alumina. Because of the formation of silver oxide and copper oxide, the size of bimetallic particles without being reduced by H₂ is between 20 to 60 nm. After being reduced, the metallic oxides turn into metallic state, so the diameter of Ag-Cu is reduced, as shown in Figure 2(b). Unfortunately, because the Ag-Cu nanoparticles are highly dispersed in alumina supports, it is impossible to distinguish the supports and the bimetallic particles from the TEM micrograph.

SEM micrographs (Figures 2(c) and 2(d)) show that the reticulate-like nanostructure is composed of much smaller materials in the presence of bimetallic particles. As catalyst carriers, the reticulate-like nanostructure makes the reactant molecules diffuse easily into the channels and contact conveniently with the internal active components.

In general, it is well known that the smaller particles are normally responsible for high catalytic activities.

FIGURE 1: N₂ adsorption-desorption isotherms with different Ag/Cu molar ratios. (a) 1/0, (b) 3/1, (c) 1/1, (d) 1/3, (e) 0/1.

3.3. XPS Spectra. We conduct an X-ray photoelectron spectroscopy (XPS) characterization of the catalysts with various Ag/Cu ratios after reduction with H₂, and the results are given in Figure 3 and Table 2. The most intense peak of Ag 3d occurs at about 368.1 eV for the pure Ag/ γ -Al₂O₃ catalyst, and the maximum binding energy of Cu 2p in the pure Cu/ γ -Al₂O₃ is 932.4 eV. Considering the sufficient pretreatment by H₂, we propose that both silver and copper are in their respective metallic state, which are confirmed by the results of IR measurement. With the increase of copper component, for the bimetallic catalyst samples, the positive peak shift (e.g., 932.4 eV $\rightarrow$ 933.7 eV) compared with pure Cu/ γ -Al₂O₃ suggests that there is an intimate contact between silver and copper, and the interaction from each other seems to give Cu a slightly greater tendency to lose electrons. Similarly, the binding energy of Ag_{3d5/2} for the bimetallic catalyst samples also has the same positive peak shift (e.g., 368.1 eV $\rightarrow$ 368.8 eV) compared with pure Ag/ γ -Al₂O₃, which means the interaction of two metals also enables Ag to exhibit a greater tendency to lose electrons [23]. At an Ag/Cu molar ratio of 1/1, the interaction between silver and copper comes to the maximum value. In summary, that the binding energy changes with the Ag/Cu molar ratios in bimetallic catalyst samples suggests that the interaction between silver and copper leads to greater tendency to lose electrons for both metals.

3.4. Microstructural Characterization. Figure 4 shows the XRD patterns of the calcined and reduced samples with various Ag/Cu ratios. All the samples contained four peaks positioned at $2\theta = 37.4^\circ$, 45.9° , 60.7° , and 67.4° , consistent with the report by He et al. [24], and correspond to (311), (400), (333), and (440) lattice planes of γ -Al₂O₃, respectively. Three peaks corresponding to the (110), (111), and (311) reflections of Ag are only visible in b and c. In addition, the peaks corresponding to Ag decrease rapidly until disappear completely with the increase of the copper content. The peaks attributable to Cu or other copper compounds do not appear at all on the copper-containing samples, which is also

TABLE 1: Chemical composition and textural properties of catalysts.

Ag/Cu (molar ratio)		ICP analysis			Pore size (nm)	Pore volume (cm ³ /g) ^b	BET surface area (m ² /g)
Nominal	EDS analysis ^a	Ag wt%	Cu wt%	Ag/Cu molar ratio			
1/0	1/0	1.52	—	1/0	16.08	1.05	261
3/1	3.17	1.34	0.31	2.55	17.17	1.37	319
1/1	1.58	1.13	0.76	0.88	18.39	1.35	293
1/3	0.42	0.65	1.22	0.31	20.51	1.48	288
0/1	0/1	—	1.89	0/1	20.68	1.67	323

^a Determined before reduction by H₂.^b Total pore volume obtained from $p/p^\circ = 0.99$.

FIGURE 2: (a) TEM image of the catalysts without reducing by H₂, $\omega = 100$ calcined at 893 K. (b) TEM image of the catalysts reduced by H₂ at 873 K, Ag/Cu = 1/1, $\omega = 100$. (c) SEM image of the reticulate-like γ -Alumina, $\omega = 100$, calcined at 893 K. (d) SEM image of the Ag-Cu/ γ -Alumina, $\omega = 100$, Ag/Cu = 1/1, reduction by H₂ at 873 K.

TABLE 2: Binding energies of catalysts determined by XPS.

Molar ratio	Ag _{3d5/2} (eV)	Ag _{3d3/2} (eV)	Cu _{2p3/2} (eV)	Cu _{2p1/2} (eV)
Ag/Cu = 1/0	368.1	374.1	—	—
Ag/Cu = 3/1	368.6	374.2	932.5	955.7
Ag/Cu = 1/1	368.8	374.4	933.7	957.1
Ag/Cu = 1/3	368.2	374.2	933.0	953.8
Ag/Cu = 0/1	—	—	932.4	953.2

noticed by another group [15]. We hypothesize that a wider diffraction peaks of Cu leads to overlapping of the diffraction peaks of alumina.

The average crystalline size of γ -Al₂O₃ and Ag-Cu mixed colloids calculated by Scherrer equation [25] is to be all less than 5 nm (Table 3). The change of Ag/Cu molar ratios has little effect on both of the crystalline size and the crystalline

phase. It is clear that the average crystalline size of the Ag-Cu mixed colloids is much smaller than the pore size of γ -Al₂O₃, which implies that the crystalline size is determined by the thermodynamics associated with the special nanostructure of the particles, rather than by the pore size of the support [26].

3.5. FT-IR Spectroscopy. Figure 5 shows FT-IR spectra of alumina and different molar ratio of Ag/Cu supported on alumina. The IR absorption peaks at 3471 cm⁻¹ and 1635~1350 cm⁻¹ for all samples are due to H-OH vibrations of H₂O, whilst the bands at 584 cm⁻¹ and 778 cm⁻¹ are attributed to Al-O vibration of γ -Al₂O₃ [27], consistent with the result of XRD. No peaks of other compounds appear in all samples, which are generally regarded as the proof of totally reduction of Ag/Cu by H₂.

3.6. Oxidation of Styrene. Styrene epoxidation catalyzed by Ag-Cu/ γ -Al₂O₃ complex at various molar ratios has been

SCHEME 1: Reaction of styrene oxidation by Ag-Cu/ γ -Al₂O₃ catalysts.TABLE 3: The crystalline size of Ag and Al₂O₃. Angle 2θ , corrected half width (β), corresponding to (111) peak of Ag and (440) peak of γ -Al₂O₃ and particles diameter “d” after Scherrer equation for Ag-Cu colloids supported on γ -Al₂O₃.

Ag/Cu	For Ag colloids			For Al ₂ O ₃ colloids		
	2θ (°)	β (°)	“d” (nm)	2θ (°)	β (°)	“d” (nm)
Al ₂ O ₃	n.c.	n.c.	n.c.	66.005	0.056	2.92
1/0	37.690	0.029	4.98	65.846	0.059	2.77
3/1	37.382	0.029	4.99	67.846	0.042	3.93
1/1	37.382	0.029	4.99	67.846	0.063	2.62
1/3	n.c.	n.c.	n.c.	65.905	0.063	2.59
0/1	n.c.	n.c.	n.c.	66.136	0.046	3.56

TABLE 4: Styrene epoxidation at different ratio of Ag/Cu supported on γ -Al₂O₃.

Entry	Ag/Cu molar ratio	Conversion (%) ^b	Selectivity (%) ^b		
			Epoxide	Benzaldehyde	Phenyl acetaldehyde
I	No catalyst	37.4	None	>99.9	c
II	γ -Al ₂ O ₃	42.1	49.6	46.6	3.8
1	Ag: Cu = 1:0/ γ -Al ₂ O ₃	89.7	65.6	34.4	c
2	Ag: Cu = 3:1/ γ -Al ₂ O ₃	93.5	76.6	23.4	c
3	Ag: Cu = 1:1/ γ -Al ₂ O ₃	94.6	66.9	33.1	c
4	Ag: Cu = 1:3/ γ -Al ₂ O ₃	87.5	62.0	38.0	c
5	Ag: Cu = 0:1/ γ -Al ₂ O ₃	83.7	20.4	79.6	c

^a Reaction conditions: Ag-Cu/ γ -Al₂O₃ catalyst 5 mg, CH₃CN 2 mL, styrene 0.5 mmol, TBHP 1.5 mmol, 82°C, 6 h.^b Determined by GC; use bromobenzene as internal standard, the correction factor is 1.27.^c Product not detected.

studied using tert-butyl hydroperoxide (TBHP) as oxidant (based on reaction Scheme 1). The mixed organic phase after reaction is sampled for off-line GC analysis, and it is confirmed that benzaldehyde and styrene oxide are the main products in this catalytic system. Using bromobenzene as internal standard, the correction factor is 1.27, and the results of the styrene oxidation are summarized in Table 4. As can be seen from the results, the conversion of styrene has been improved with addition of either Ag or Cu. In contrast, in the simultaneous presence of copper and silver, that is, Ag-Cu bimetallic catalysts, much higher catalytic activity was shown than that of the corresponding monometallic silver or copper supported on γ -Al₂O₃ catalysts. It is proposed that the addition of copper can help to improve the conversion of styrene, whereas the role of silver is to adjust the selectivity of styrene epoxide. Therefore, the selectivity of styrene epoxide can be controlled by adjusting the Ag/Cu molar ratio. The maximum selectivity of styrene epoxide (up to 76.6%) appears at Ag/Cu molar ratio of 3/1, as the conversion of styrene is up to 93.5%. Additionally, owing to the maximum value of the interaction between silver and copper at Ag/Cu molar ratio of 1/1, the maximum conversion (94.6%) appears. A possible mechanism may be that

peroxidic oxygen adsorbs on Ag, while styrene molecules are adsorbed on the crystal surface of Cu; initial complex formation between bimetallic catalyst and tert-butyl hydroperoxide renders the peroxidic oxygen more electrophilic and hence more labile to attack by an olefinic double bond [6]; meanwhile, XPS results demonstrate that the silver and copper components are in intimate contact with each other so that the O₂⁻ adsorbed on the silver surface can migrate to the copper surface and react with the adsorbed styrene easily. However, on the basis of the ratio of 1/1, further larger copper content causes lower conversion, styrene oxide selectivity for Cu is more metallic activity than Ag, and a number of copper oxides might be formed during the reaction process for the excess oxidant. Then, the presence of copper oxides perhaps prevent the further reaction [28], and wherefore Cu shows the lowest conversion, and the conversion of 1/3(Ag/Cu) catalyst is lower than that of Ag/Cu at the ratio of 1/0. In addition, the styrene oxide selectivity decreases with addition of copper component from Ag/Cu molar ratio of 3/1 to 1/3, which may be attributed to the unstable styrene oxide product in the presence of massive copper. In such conditions, the oxidation of metallic Cu by styrene oxide perhaps becomes a favored reaction.

FIGURE 3: XPS spectra of Ag-Cu/ γ -alumina with different Ag/Cu molar ratios.

4. Conclusions

In summary, we have developed a microemulsion method for loading Ag-Cu bimetallic nanoparticles confined in γ -alumina at room temperature, and the physicochemical properties have been investigated. Detailed studies by XRD, TEM, and SEM methodology reveal that the new Ag-Cu bimetallic nanoparticles supported on the reticulate-like γ -alumina distribute evenly and have smaller size. It is interinteresting to note that there is an interaction between silver and copper that makes both metals have a greater tendency to lose electrons. Furthermore, high activity in the oxidation of styrene is observed using the synthesized materials as catalysts, which may be due to the

FIGURE 4: Wide-angle XRD patterns of γ - Al_2O_3 and Ag-Cu bimetallic nanoparticles supported on γ - Al_2O_3 at various molar ratios. [Metal salts]/[$\text{N}_2\text{H}_5\text{OH}$] = 1/10; ω = 100; reaction time = 2.5 h; All samples were reduced by H_2 at 873 K and γ - Al_2O_3 was calcined at 893 K.

FIGURE 5: FTIR spectra of alumina and different molar ratio of Ag/Cu supported on alumina.

interaction between silver and copper: Ag plays a key role in adsorption of O_2^- and mainly catalyzes styrene epoxidation to styrene epoxide. Instead, Cu provides more active sites for adsorbing styrene, whilst O_2^- adsorbed on the silver surface can migrate to the copper surface and react with the adsorbed styrene easily. So, the selectivity of styrene oxide has a close relationship with the amount of Ag and can be controlled by adjusting molar ratio of Ag/Cu. In addition, the minimum consumption of noble metals makes the catalysts

cost effective. Bimetallic catalysts prepared herein may also be promising candidates for applications in many other reactions such as in CO oxidation.

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References

- [1] C.-W. Yen, M.-L. Lin, S.-A. Wang, S.-A. Chen, J.-M. Chen, and C.-Y. Mou, "CO oxidation catalyzed by Au-Ag bimetallic nanoparticles supported in mesoporous silica," *Journal of Physical Chemistry C*, vol. 113, no. 41, pp. 17831–17839, 2009.
- [2] M. Enever, S. Linic, K. Uffalussy, J. M. Vobs, and M. A. Barteau, "Synthesis, structure, and reactions of stable oxametallacycles from styrene oxide on Ag(111)," *Journal of Physical Chemistry B*, vol. 109, no. 6, pp. 2227–2233, 2005.
- [3] J.-H. Liu, A.-Q. Wang, Y.-S. Chi, H.-P. Lin, and C.-Y. Mou, "Enhancing stability and oxidation activity of cytochrome c by immobilization in the nanochannels of mesoporous aluminosilicates," *Journal of Physical Chemistry B*, vol. 109, no. 25, pp. 40–43, 2005.
- [4] K. Arve, K. Svennerberg, F. Klingstedt et al., "Structure-activity relationship in HC-SCR of NO_x by TEM, O₂-chemisorption, and EDXS study of Ag/Al₂O₃," *Journal of Physical Chemistry B*, vol. 110, no. 1, pp. 420–427, 2006.
- [5] Z.-M. Wang, M. Yamaguchi, I. Goto, and M. Kumagai, "Characterization of Al₂O₃ de-NO(x) catalysts by probing surface acidity and basicity of the supporting substrate," *Physical Chemistry Chemical Physics*, vol. 2, no. 13, pp. 3007–3015, 2000.
- [6] E. Zhan, Y. Li, J. Liu, X. Huang, and W. Shen, "Corrigendum to "A VO_x/meso-TiO₂ catalyst for methanol oxidation to dimethoxymethane" [Catal. Commun. 10 (2009) 2051–2055]," *Catalysis Communications*, vol. 11, no. 3, p. 225, 2009.
- [7] J. T. Roberts and R. J. Madix, "Epoxidation of olefins on silver: conversion of norbornene to norbornene oxide by atomic oxygen on Ag(110)," *Journal of the American Chemical Society*, vol. 110, no. 25, pp. 8540–8541, 1988.
- [8] J. J. Cowell, A. K. Santra, and R. M. Lambert, "Ultrasensitive epoxidation of butadiene on Cu111 and the effects of Cs promotion," *Journal of the American Chemical Society*, vol. 122, no. 10, pp. 2381–2382, 2000.
- [9] J. J. Cowell, A. K. Santra, R. Lindsay, R. M. Lambert, A. Baraldi, and A. Goldoni, "Bonding and reactivity of styrene on Cu(110): heterogeneous alkene epoxidation without the use of silver," *Surface Science*, vol. 437, no. 1, pp. 1–8, 1999.
- [10] J. H. Sinfelt, "Supported "bimetallic cluster" catalysts," *Journal of Catalysis*, vol. 29, no. 2, pp. 308–315, 1973.
- [11] N. Toshima, M. Harada, T. Yonezawa, K. Kushihashi, and K. Asakura, "Structural analysis of polymer-protected Pd/Pt bimetallic clusters as dispersed catalysts by using extended X-ray absorption fine structure spectroscopy," *Journal of Physical Chemistry*, vol. 95, no. 19, pp. 7448–7453, 1991.
- [12] X. Wang, N. Li, L. D. Pfefferle, and G. L. Haller, "Pt-Co bimetallic catalyst supported on single-walled carbon nanotubes: effect of alloy formation and oxygen containing groups," *Journal of Physical Chemistry C*, vol. 114, no. 40, pp. 16996–17002, 2010.
- [13] L. Zhao, K. Fang, D. Jiang, D. Li, and Y. Sun, "Sol-gel derived Ni-Mo bimetallic carbide catalysts and their performance for CO hydrogenation," *Catalysis Today*, vol. 158, no. 3-4, pp. 490–495, 2010.
- [14] V. V. Agrawal, P. Mahalakshmi, G. U. Kulkarni, and C. N. R. Rao, "Nanocrystalline films of Au-Ag, Au-Cu, and Au-Ag-Cu alloys formed at the organic-aqueous interface," *Langmuir*, vol. 22, no. 4, pp. 1846–1851, 2006.
- [15] L. Gang, B. G. Anderson, J. Van Grondelle et al., "Alumina-supported Cu-Ag catalysts for ammonia oxidation to nitrogen at low temperature," *Journal of Catalysis*, vol. 206, no. 1, pp. 60–70, 2002.
- [16] X. Yang, S. Gao, and Z. Xi, "Reaction-controlled phase transfer catalysis for styrene epoxidation to styrene oxide with aqueous hydrogen peroxide," *Organic Process Research & Development*, vol. 9, no. 3, pp. 294–296, 2005.
- [17] D.-H. Chen and C.-J. Chen, "Formation and characterization of Au-Ag bimetallic nanoparticles in water-in-oil microemulsions," *Journal of Materials Chemistry*, vol. 12, pp. 1557–1562, 2002.
- [18] L. Qi, J. Ma, and J. Shen, "Synthesis of copper nanoparticles in nonionic water-in-oil microemulsions," *Journal of Colloid and Interface Science*, vol. 186, no. 2, pp. 498–500, 1997.
- [19] H. Liu, X. Du, P. Gao, J. Zhao, J. Fang, and W. Shen, "Distinct magnetic properties of one novel type of nanoscale cobalt-iron Prussian blue analogues synthesized in microemulsion," *Journal of Magnetism and Magnetic Materials*, vol. 322, no. 5, pp. 572–577, 2010.
- [20] L. Tian, *Study on the preparation of γ -alumina nanomaterials by microemulsion and microemulsion hydrothermal synthesis*, M.S. thesis, Lanzhou University, Lanzhou, China, 2008.
- [21] H. H. Ingelsten, J.-C. Béziat, K. Bergkvist et al., "Deposition of platinum nanoparticles, synthesized in water-in-oil microemulsions, on alumina supports," *Langmuir*, vol. 18, no. 5, pp. 1811–1818, 2002.
- [22] J. Zhao, L. Tian, J. Fang, and W. Shen, "China patent 200810093754.0," 2008.
- [23] A.-Q. Wang, J.-H. Liu, S.D. Lin, T.-S. Lin, and C.-Y. Mou, "A novel efficient Au-Ag alloy catalyst system: preparation, activity, and characterization," *Journal of Catalysis*, vol. 233, no. 1, pp. 186–197, 2005.
- [24] Z. He, A. Zhang, S. Song et al., " γ -Al₂O₃ modified with praseodymium: an application in the heterogeneous catalytic ozonation of succinic acid in aqueous solution," *Industrial and Engineering Chemistry Research*, vol. 49, no. 24, pp. 12345–12351, 2010.
- [25] B. E. Warren, *X-Ray Diffraction*, Addison-Wesley, Reading, Mass, USA, 1969.
- [26] X. Liu, A. Wang, X. Wang, C.-Y. Mou, and T. Zhang, "Au-Cu Alloy nanoparticles confined in SBA-15 as a highly efficient catalyst for CO oxidation," *Chemical Communications*, no. 17, pp. 3187–3189, 2008.
- [27] S. Ramesh, E. Sominska, B. Cina, R. Chaim, and A. Gedanken, "Nanocrystalline γ -alumina synthesized by sonochemical hydrolysis of

alkoxide precursor in the presence of organic acids: structure and morphological properties," *Journal of the American Ceramic Society*, vol. 83, no. 1, pp. 89–94, 2000.

- [28] J. R. Monnier and G. W. Hartley, "Phase transition in Langmuir films of octadecylmalonic acid," *Journal of Catalysis*, vol. 203, no. 2, pp. 529–531, 2001.