Synthesis and evaluation of ruthenium–copper oxide/silica catalysts derived from microemulsion processing

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Bimetallic Ru–Cu catalysts supported on SiO_2 have been synthesized in microemulsions using sodium metasilicate (Na_2SiO_3), copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) and ruthenium chloride ($RuCl_3$) at 28 °C. The microemulsion system consists of sodium 1,4-bis(2-ethylhexyl) sulfosuccinate (AOT) and sodium dodecyl sulphate (SDS), cyclohexane, and an aqueous solution of sodium metasilicate or metal salts. The catalysts have been characterized by XPS, EDX/SEM with line scanning and they possess a very narrow pore size distribution (around 38 Å) and relatively high specific surface areas (around 400 m^2/g). The catalytic results of the N_2O decomposition reveal that higher conversions of N_2O can be achieved by the catalysts synthesized from the microemulsion process at lower temperatures (around 400 °C).

Keywords: microemulsion synthesis, ruthenium or copper catalysts, N_2O decomposition, mesopores, surface area

1. Introduction

The microemulsion processing of polymers and ceramics has attracted great attention recently [1–11]. A microemulsion is generally defined as a system composed of a mixture of water or brine, hydrocarbon(s) and amphiphilic compound(s) in the form of a thermodynamically stable and optically isotropic solution [4]. The term amphiphiles refers to surfactants as well as co-surfactants, such as a short chain alcohol. A transparent microemulsion can be formed as droplets of oil-swollen micelles dispersed in water (known as oil-in-water (o/w) microemulsion), or water-swollen micelles dispersed in oil (known as water-in-oil (w/o) microemulsion). In between o/w and w/o microemulsion regions, there may exist bicontinuous microemulsions, where oil and water domains are randomly interconnected to form sponge-like nanostructures. In any case, the size of nanostructures in microemulsions may range from about 5 to 70 nm. Due to these unique nanosized structures, microemulsion processing is deemed to be a novel method for producing nanostructural materials, such as polymers, inorganic materials and inorganic/polymer nanocomposites [12].

Spherical silica particles of nanosizes can be prepared by hydrolysis of sodium metasilicate [13]. Ultrafine silica powders have been prepared from sodium orthosilicate (Na_4SiO_4) and sodium metasilicate (Na_2SiO_3) in microemulsion stabilized by a mixture of nonionic surfactants [13,14]. The specific surface area of silica produced in a microemulsion can be as high as 500 m^2/g. In addition, silica–copper oxide composites have also been prepared by microemulsion to have the specific surface area ranging from 200 to 400 m^2/g and a relatively narrow size (3–6 nm) distribution of mesopores [15].

The aim of this study is to use microemulsion for synthesizing some silica-based catalysts with promising surface characteristics and catalytic activities. Here we report the preparation and characterization of Ru–Cu/silica catalysts obtained from microemulsion and the catalytic activities of the catalysts in the decomposition of N_2O. Nitrous oxide (N_2O) is selected for the catalytic study because of the concern of environmental pollution by this gas. A large number of catalysts such as metal oxides, mixed oxides, perovskite-type oxide, hydrotalcites and transition-metal-exchanged zeolites had been used for N_2O decomposition at elevated temperatures [16–20].

2. Experimental

2.1. Materials

Chemically pure (>98 wt%) sodium metasilicate (Na_2SiO_3) (Hanawa), cyclohexane (>99.5%) (Merck), sodium 1,4-bis(2-ethylhexyl) sulfosuccinate (AOT) (Sigma), $RuCl_3 \cdot 3H_2O$ (BDH), cupric nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) (BDH), sodium dodecyl sulfate (SDS) (BDH), poly(oxyethylene)$_5$ nonylphenol ether (NP-5) and poly(oxyethylene) nonylphenol ether (NP-9) from Albright and Wilson Asia were all used in the forms as received. Water was distilled twice.

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2.2. Synthesis of silica and its catalysts via single-step microemulsion process

The single-step microemulsion process requires one microemulsion solution (designated as MA) and one external aqueous solution containing acid or metal salts (designated as AQ). MA contained three basic components, i.e., 12 wt% surfactant AOT and 4 wt% SDS, 48 wt% cyclohexane and 36 wt% aqueous solution of sodium metasilicate (0.2 M). The external aqueous solution AQ required to produce silica is HCl (0.4 M) and that required to produce silica-supported Ru–Cu oxide is a mixture of $Cu(NO_3)_2$ (0.1 M) and $RuCl_3$ (0.01 M). During the single-microemulsion processing, the external aqueous solution AQ was added dropwise into MA at 28 °C with continuous stirring until the system progressively became gel. After 24 h, the gel was recovered by centrifugation. The gel was then extracted with ethanol using a soxhlet extractor for 48 h to remove the surfactants AOT and SDS. The extent of the surfactant removal was checked by infrared (IR) measurements. The gel was then dried at 100 °C in an oven for 8 h followed by the calcination at 400 °C for 12 h. Depending on the contents of the external aqueous solutions, the dried samples can be pure silica or silica containing metal oxides. For example, the preparation of silica catalyst SC2 (table 1) requires the aqueous solution of AQ to contain 18 wt% copper nitrate (0.1 M), 18 wt% $RuCl_3$ (0.01 M) and 15 wt% HCl (0.4 M) based on the weight of microemulsion MA. After mixing MA with AQ, the gel composite was washed and dried as mentioned above. The metal oxide/silica catalyst is denoted as sample SC1 (containing Cu only) or SC2 (containing both Cu and Ru oxides), as summarized in table 1.

2.3. Preparation of the catalyst with silica support

Ruthenium–copper oxide catalyst (CS1) was also prepared using pre-synthesized silica support S1, as listed in table 1. The suspension solution of the silica support was prepared by dispersing 0.75 g of powder S1 in 20 ml of deionized water under ultrasonification. To the suspension solution, 20 ml of $RuCl_3{\cdot}3H_2O$ (0.01 M) and 3 ml of $Cu(NO_3)_2{\cdot}3H_2O$ (0.1 M) were added dropwise under continuous stirring. The powder was recovered by centrifugation and washed with deionized water for several times. The catalyst CS1 obtained was dried at 100 °C overnight followed by calcination at 400 °C for 12 h.

2.4. Catalyst characterization

The infrared (IR) spectra of the catalyst powder in the form of KBr pellet were recorded with a FTIR spectrometer (Perkin–Elmer, model 1600 series). Inductively coupled plasma/atomic emission spectrometry (ICP/AES) was used to determine the element contents in the catalyst with a Plasmascan 710 (Lab Tan Company).

A scanning electron microscope (SEM, Hitachi 5800) was used to examine the catalyst particles. The elemental distribution in the catalyst particles was determined using EDX/SEM (Oxford/Jeol) line scanning. The line scale ranging from 100 to 200 μm across the sample surface was scanned by SEM followed by EDX analysis.

The X-ray photoelectron spectroscopic studies (XPS) of the catalyst were carried out by a VG-ESCA-LAB 2201-XL using MKII spectrometer radiation (1253.6 eV, 120 W) at a constant analyzer pass energy of 20 eV. All the binding energy (BE) were calibrated with respect to the standard C 1s (284.6 eV) and curve fitting analysis with Gaussian shape was performed.

Specific surface areas of calcined catalyst powders were determined by the Brunauer–Emmett–Teller (BET) N_2 adsorption using a NOVA 1000 analyser (Quantachrome Corporation). About 20–80 mg of samples were treated at 350 °C for 2 h prior to the measurements. In order to check whether the structure of the catalyst was destroyed during the reaction, the specific surface area and pore size distribution of the catalyst after reaction were re-determined.

2.5. Catalyst evaluation

Ru–Cu oxide/silica catalyst powder (40–60 mesh) was pelletized before use in order to reduce the effect of pressure drop in the packed-bed reactor. About 0.2 g of the catalyst was loaded in a packed-bed microreactor and pretreated at 400 °C for 90 min in a flow of nitrogen (25% in helium) to remove all absorbed moisture.

N_2O decomposition reaction was carried out using a continuous flow of N_2O (10 vol% in helium); the total flow rate used for reaction was about 27 ml/min, yielding a space velocity of 4000 h^{-1}. The temperature of the reactor bed was monitored using a thermocouple and the flow rate of N_2O was measured by four mass flow controllers (Gossen 5975). The gas mixtures before and after catalytic reaction were analyzed on line by HP 6890 GC using a thermal

Table 1
Synthesis of silica and its catalysts via microemulsion processing.

Sample	Contents for MA (wt%)			Aqueous solution of 0.2 M	Aqueous solution of acid or metal salts AQ (based on the weight of MA) (wt%)			Elemental analysis after drying at 100 °C (wt%)				Peak particle
	Cyclohexane	AOT	SDS	Na_2SiO_3 for MA (wt%)	HCl (0.4 M)	$Cu(NO_3)_2$ (0.1 M)	$RuCl_3$ (0.01 M)	Si	Cl	Cu	Ru	size (nm)
S1	48	12	4	36	36	–	–	34.12	0.01	–	–	25
SC1	48	12	4	36	20	36	–	31.32	0.03	5.61	–	32
SC2	48	12	4	36	15	18	18	32.53	0.32	3.25	1.59	34
CS1:	0.75 g silica S1 + 20 ml H_2O + 3 ml 0.1 M $Cu(NO_3)_2$ + 20 ml 0.01 M $RuCl_3$							34.15	0.35	3.51	1.61	36

conductivity detector. The GC column used was Porapak Q (4 m long and the outer diameter is 1/8 inches). The oven temperature of the GC was 80 °C and helium gas was the carrier gas with a flow rate of 25 ml/min. The catalytic activity was evaluated based on N_2O conversion.

3. Results and discussion

3.1. Synthesis of catalysts

For the comparison of the performance of the SC2 catalyst prepared by a single-step microemulsion process, the similar catalyst CS1 was also prepared using pre-synthesized silica support S1. With the single-step microemulsion process, the aqueous solution containing Cu salt (for SC1) or both Ru and Cu salts (for SC2) was directly added into the microemulsion, where the hydrolysis and condensation of sodium metasilicate (Na_2SiO_3) take place. Since the hydrolysis of sodium metasilicate began upon the addition of the salt solution due to its acidity, the salt hydrolysis and metal deposition might occur simultaneously. On the other hand, silica support S1 was mixed with the same aqueous solution of Ru and Cu salts to produce catalyst CS1.

Based on the elemental analyses as listed in table 1, the Cu and Ru contents in catalyst SC2 are 3.25 and 1.59 wt%, respectively. These values are comparable to those from catalyst CS1, i.e., 3.51 and 1.61 wt%, respectively. The particle sizes (34–36 nm) for both catalysts SC2 and CS1 are also similar.

3.2. Catalyst characterization

The EDX mapping technique with line-scanning was performed on the catalyst surface at micron range. The elemental line-scanning spectra of Si, O, Cu and Ru for the catalyst SC2 exhibited uniform elemental distributions, as shown in figure 1. However, the elemental distribution on the surface of catalyst CS1 is not as uniform as that of catalyst SC2.

Figure 2 shows the XPS scanning spectra of the synthesized catalysts. Cu peaks can be clearly seen from the surfaces of catalysts SC2 and CS1. Since the binding energy of Ru (around 281 eV) overlaps with that of C 1s

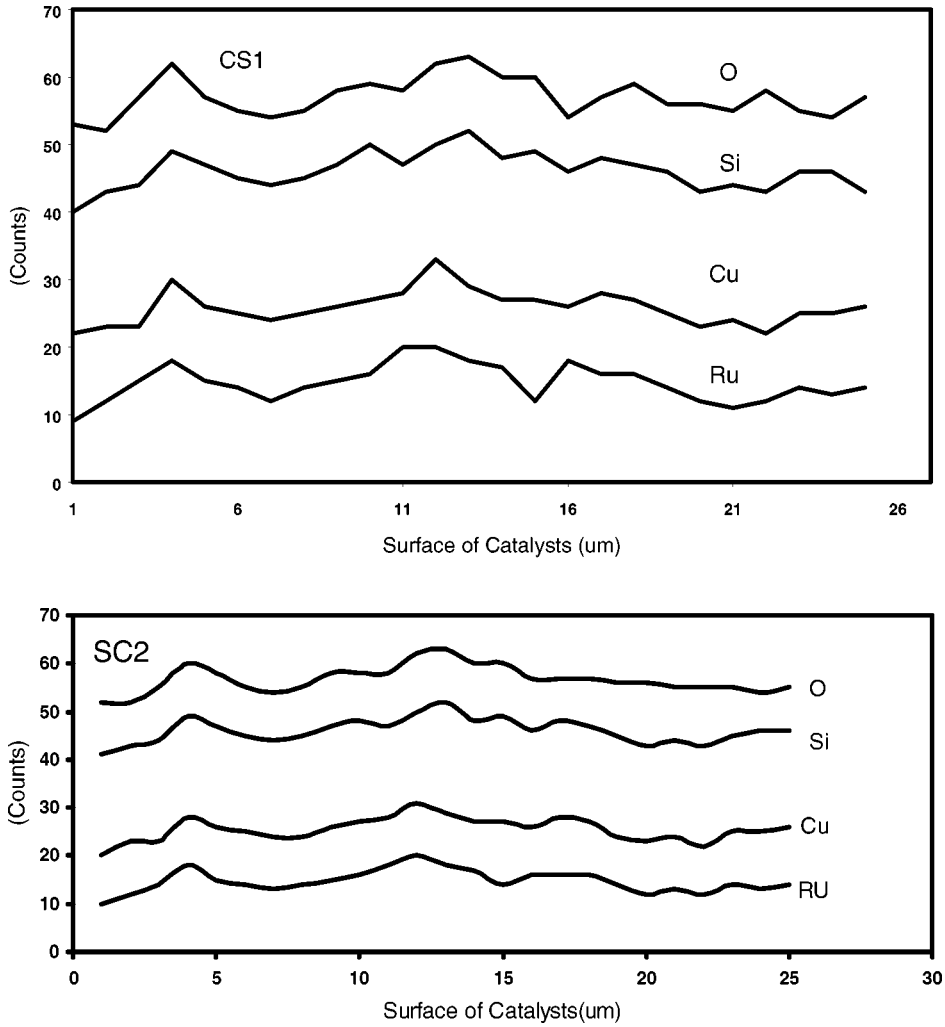

Figure 1. Elemental distribution of catalyst surface by line-scanning mapping for SC2 and CS1.

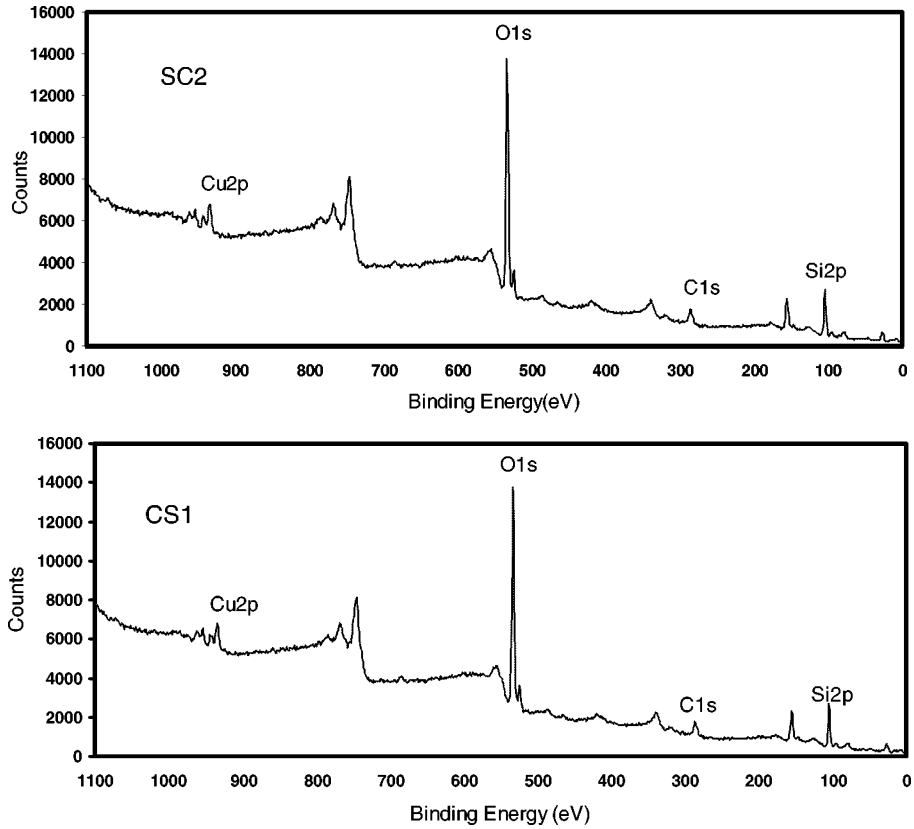

Figure 2. XPS scanning spectra of catalysts SC2 and CS1.

Table 2
Some characteristics of catalysts.

Materials	Specific surface area (m^2/g)	Peak pore diameter (Å)	Pore volume (ml/g)
Support material:			
S1 silica (calcined at 400 °C)	458.3	32.1	0.31
Synthesized catalysts:			
SC2 (calcined at 400 °C)	408.5	38.4	0.25
CS1 (calcined at 400 °C)	198.1	86.5	0.23
Catalysts after catalytic reactions at 400 °C:			
SC2	413.6	37.4	0.20
CS1	92.5	109.2	0.21

(around 284 eV), it is difficult to resolve the tiny Ru peak out from the large peak of C 1s (figure 3). For catalyst SC2, Ru might possibly exist as RuO_2 [21] according to the resolved binding energy. The resolved peaks of Cu 2p indicate that catalysts CS1, and SC2 might consist of CuO and Cu_2O [21].

The specific surface area of S1 silica (458.3 m^2/g) reduced markedly to 198.1 m^2/g when it was impregnated to become catalyst CS1 (table 2). Figure 4 shows the rather narrow pore size distribution (3–5 nm) for catalyst SC2. Its peak pore size (3.8 nm) remained about the same (3.7 nm) even after the catalytic reaction for N_2O. However, the peak pore sizes were much larger for catalyst CS1 (8.7 nm) and it further increased to 10.9 nm after catalytic reactions (table 2). This was also accompanied by a significant reduction in the specific area from 198.1 to 92.5 m^2/g for CS1 after catalytic reaction at 400 °C. It shows that the least modification of pore structures occurred in catalyst CS2 as compared to that of catalyst SC1 during catalytic reactions. The one-step microemulsion process is thus a promising synthetic method for producing a catalyst of good surface characteristics.

3.3. Catalytic performance

The decomposition of N_2O was carried out to evaluate the performance of the synthesized catalysts at different temperatures (table 3). The SC1 catalyst (table 1) containing Cu only did not show any obvious catalytic activity, indicating that the active site for the catalyst containing sin-

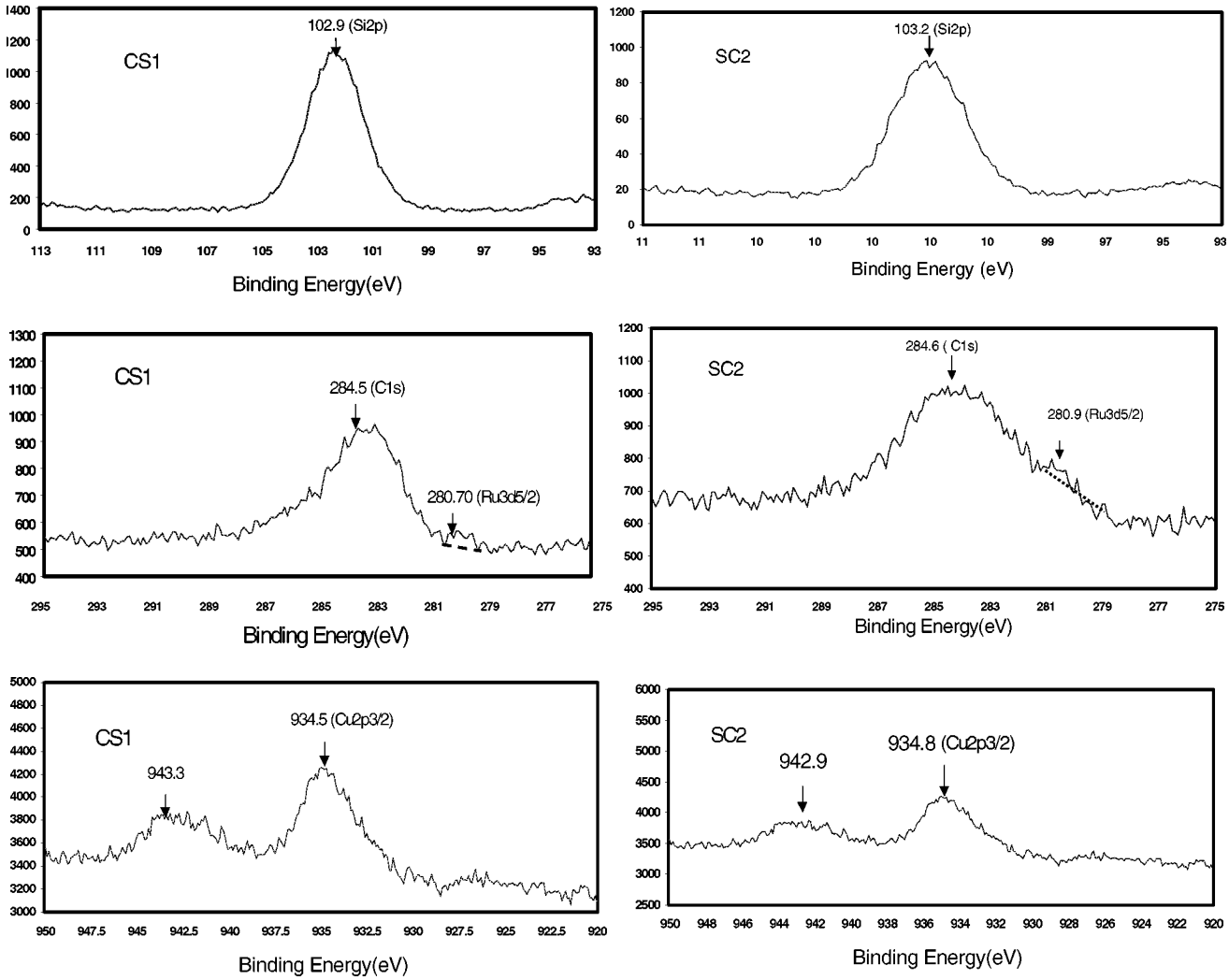

Figure 3. XPS elemental binding energy from resolved spectra of catalysts SC2 and CS1.

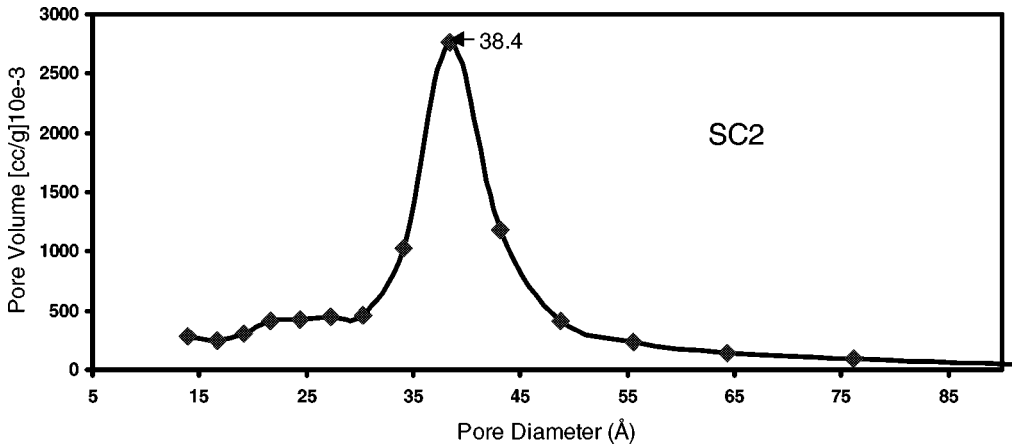

Figure 4. The pore size distributions of catalyst SC2.

gle metal Cu is not suitable for N_2O decomposition. But catalyst SC2 could convert 98.2% of N_2O to N_2 and O_2 at 400 °C as compared to 94.1% for catalyst CS1. The results in table 3 show that catalyst SC2 synthesized through the single-step microemulsion process was superior to catalyst CS1 towards N_2O decomposition at lower reaction temperatures ranging from 400 to 450 °C.

It is suggested that the combination of silica and metal species in the aqueous phase of a microemulsion may have resulted in some molecular interactions between sil-

Table 3
Decomposition of N_2O by Ru–Cu oxide/silica catalysts.

Reaction T (°C)	SC2 (vol%)	CS1 (vol%)
250	5.9	3.1
300	7.5	3.8
350	70.6	64.0
400	98.2	94.1
450	100	97.2
500	100	100

ica species and Ru^{3+}/Cu^{2+} during the synthesis. This would then make possible the uniform incorporation of metal species in the framework of silica, leading to the stability of the supported metal species on the silica catalyst prepared from the microemulsion processing.

4. Conclusions

The single-step microemulsion processing has been successfully used to synthesize Ru–Cu oxides as catalysts supported by silica through the controlled hydrolysis/polymerization of sodium metasilicate (Na_2SiO_3), copper nitrate ($Cu(NO_3)_2{\cdot}3H_2O$) and ruthenium chloride ($RuCl_3$) at room temperature. The microemulsion system consists of surfactants AOT and SDS, cyclohexane, and an aqueous solution of sodium metasilicate or metal salts. A higher specific surface area (around 400 m^2/g) and rather uniform pore size (around 38 Å) of the catalyst prepared from the microemulsion could be well maintained during the catalytic reaction. The catalyst was found to have very high catalytic activity for the decomposition of N_2O at relatively low reaction temperatures (around 400 °C). The XPS and SEM/line scanning results show that an uniform elemental distribution of RuO_2 on the SiO_2 (with a trace loading of CuO/Cu_2O) could be obtained by this microemulsion processing.

References

[1] K. Holmberg, Adv. Colloid Interface Sci. 51 (1994) 137.
[2] M.J. Schwuger and K. Stickdorn, Chem. Rev. 95 (1995) 849.
[3] L.M. Gan and C.H. Chew, in: *Polymer Materials Encyclopeda*, ed. J.C. Salamone (CRC Press, Boca Raton, FL, 1996) pp. 4321–4331.
[4] B.K. Palu and S.P. Moulike, J. Dispersion Sci. Technol. 18 (1997) 301.
[5] F. Candau and J.Y. Anquetil, in: *Micells, Microemulsions and Monolayers*, ed. D.O. Shah (Dekker, New York, 1998) pp. 193–213.
[6] L.M. Gan, L.H. Zhang, H.S.O. Chan, C.H. Chew and B.H. Loo, J. Mater. Sci. 31 (1996) 1071.
[7] W.R. Palani, M. Raj, M. Sasthav and J. Cheung, J. Appl. Polym. Sci. 47 (1993) 499.
[8] L.M. Gan, T.H. Chieng, C.H. Chew and S.C. Ng, Langmuir 12 (1996) 319.
[9] H. Yamauchi, T. Ishikawa and S. Kondo, Colloids Surf. 37 (1989) 71.
[10] G.K. Lim, J. Wang, S.C. Ng, C.H. Chew and L.M. Gan, Biomaterials 18 (1997) 1433.
[11] B.P. Lim, J. Wang, S.C. Ng, C.H. Chew and L.M. Gan, Ceram. Int. 24 (1998) 205.
[12] L.M. Gan and C.H. Chew, in: *Advanced Functional Molecules and Polymers*, ed. H.S. Nalwa (Gordon and Breach, New York, 1999), to appear.
[13] L.M. Gan, K. Zhang and C.H. Chew, Colloids Surf. A 110 (1996) 199.
[14] K. Zhang, L.M. Gan, C.H. Chew and L.H. Gan, Mater. Chem. Phys. 47 (1997) 164.
[15] K. Zhang, C.H. Chew, G.Q. Xu, J. Wang and L.M. Gan, Langmuir 15 (1999) 3056.
[16] A. Kudo and H. Nayayoshi, Catal. Lett. 52 (1998) 109.
[17] P. Ciambelli, A. Di Benedetto, E. Garufi, R. Pirone and G. Russo, J. Catal. 175 (1998) 161.
[18] H. Dandl and G. Emig, Appl. Catal. A 168 (1998) 261.
[19] T. Turek, J. Catal. 174 (1998) 98.
[20] J. Obuchi, Oi, A. Ogata, G.R. Bamwenda, R. Tanaka, T. Hibino and S. Kushiyama, Appl. Catal. B 13 (1998) 197.
[21] C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder and G.E. Muilenberg, eds., *Handbook of X-Ray Photoelectron Spectroscopy* (Perkin–Elmer Corporation, Eden Prairie, MN, 1979).