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Rh₂O₃/mesoporous MO_x-Al₂O₃ (M = Mn, Fe, Co, Ni, Cu, Ba) catalysts: Synthesis, characterization, and catalytic applications

Huan Liu, Yi Lin, Zhen Ma*

Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention (LAP3), Department of Environmental Science and Engineering, Fudan University, Shanghai 200433, China

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ABSTRACT

Recently, a one-pot self-assembly method was proposed for the synthesis of mesoporous Al₂O₃ and MO_x-Al₂O₃ composite materials. However, few attempts have been made to use mesoporous MO_x-Al₂O₃ composites to support metal oxides for catalysis. In the present work, mesoporous MO_x-Al₂O₃ (M = Mn, Fe, Co, Ni, Cu, Ba) materials were prepared by a one-pot self-assembly method using Pluronic P123 as a structure-directing agent. The obtained mesoporous materials were loaded with Rh₂O₃ nanoparticles via impregnation with Rh(NO₃)₃ followed by calcination in air at 500 °C. The resulting catalysts were characterized by X-ray diffraction, N₂ adsorption-desorption measurements, transmission electron microscopy, inductively coupled plasma optical emission spectrometry, X-ray photoelectron spectroscopy, and their catalytic activity and stability for CO oxidation and N₂O decomposition were tested. The Rh₂O₃ nanoparticles were found to be on the order of 1 nm in size and were highly dispersed on the high surface area mesoporous MO_x-Al₂O₃ supports. A number of the Rh₂O₃/mesoporous MO_x-Al₂O₃ catalysts exhibited higher catalytic activity than the Rh₂O₃/mesoporous Al₂O₃ prepared for comparison.

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1. Introduction

Since the development of mesoporous SiO₂ in the 1990s [1,2], the synthesis and catalytic application of mesoporous SiO₂-based materials have attracted much attention in the catalysis community [3–7]. Mesoporous SiO₂ materials have ordered nanopores, large surface area, and high thermal stability, which make them ideal for fabricating supported or other functionalized catalysts for a wide range of useful reactions.

In recent years, mesoporous metal oxides such as TiO₂, Co₃O₄, and Al₂O₃ have attracted great interest because they have unique functionalities associated with their redox and/or acid properties [8–10]. Nevertheless, owing to the lower thermal stability and higher density of these metal oxides com-

pared with those of SiO₂, the synthesis of high-surface-area mesoporous metal oxides constitutes a significant challenge.

Al₂O₃ is one of the most useful industrial catalysts and supports [11]. Al₂O₃-supported metal or metal oxide catalysts have found wide applications in the processing of fossil and biomass fuels, the conversion of chemical stocks into useful chemical products, and the cleaning up of air. A number of advances have been made in the synthesis of mesoporous Al₂O₃ [12–19]. In particular, a simple solvent evaporation-induced self-assembly (EISA) strategy has been developed for the synthesis of ordered mesoporous Al₂O₃ [18]. A similar method was later used for the synthesis of mesoporous MgO-Al₂O₃ [19,20], CaO-Al₂O₃ [19,21], TiO₂-Al₂O₃ [19,22,23], CrO_x-Al₂O₃ [19,24], NiO-Al₂O₃ [25], ZrO₂-Al₂O₃ [26,27], LaO_x-Al₂O₃ [28], and CeO₂-Al₂O₃ [29].

* Corresponding author. Tel: +86-21-65642997; Fax: +86-21-65643597; E-mail: zhenma@fudan.edu.cn

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The development of mesoporous $\text{MO}_x\text{-Al}_2\text{O}_3$ has provided new opportunities for catalysis. First, mesoporous $\text{MO}_x\text{-Al}_2\text{O}_3$ materials themselves can be used as catalysts. For example, mesoporous $\text{CrO}_x\text{-Al}_2\text{O}_3$ has shown high catalytic activity and stability for the liquid phase oxidation of cyclohexane [24], and mesoporous $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ has shown good performance in the dehydrogenation of ethane and propane [30].

Alternatively, mesoporous $\text{MO}_x\text{-Al}_2\text{O}_3$ materials can be used as precursors for making active catalysts after proper pretreatment. For example, mesoporous $\text{CoO}_x\text{-Al}_2\text{O}_3$ was reduced in H_2 to produce $\text{Co}/\text{mesoporous Al}_2\text{O}_3$ active for partial oxidation of methane [31]. Mesoporous $\text{CuO}_x\text{-Al}_2\text{O}_3$ was transformed into $\text{Cu}/\text{mesoporous Al}_2\text{O}_3$ active for direct synthesis of dimethyl ether [32] and ethanol synthesis via dimethyl oxalate hydrogenation [33]. Mesoporous $\text{NiO-Al}_2\text{O}_3$ [34–36], $\text{NiO-MgO-Al}_2\text{O}_3$ [37,38], $\text{NiO-CaO-Al}_2\text{O}_3$ [39], $\text{NiO-LaO}_x\text{-Al}_2\text{O}_3$ [40], and $\text{NiO-CeO}_2\text{-Al}_2\text{O}_3$ [40–42] were reduced to form metallic Ni nanoparticles supported on their Al_2O_3 -based mesoporous matrix, and their catalytic performance for the CO_2 reforming of methane was tested. Mesoporous $\text{NiO-Al}_2\text{O}_3$ was reduced to form supported Ni catalysts for selective CO methanation [43], partial oxidation of methane to syngas [44], and steam reforming of CH_4 [45]. Ni/mesoporous $\text{ZrO}_2\text{-Al}_2\text{O}_3$ [46] and Ni/mesoporous $\text{MgO-Al}_2\text{O}_3$ [47] prepared by one-pot synthesis of mesoporous mixed oxides followed by reduction in H_2 were used for steam reforming of ethanol [46] and methane [47], respectively. The advantage of this preparation method (one-pot synthesis followed by reduction) is that the metallic nanoparticles can be highly dispersed on the internal surfaces of the mesoporous oxide matrix, and their catalytic activity may be further tuned by the presence of another metal oxide (other than Al_2O_3).

Although mesoporous Al_2O_3 has been occasionally used to support metals or metal oxides [48–52], the employment of mesoporous $\text{MO}_x\text{-Al}_2\text{O}_3$ materials as supports for the preparation of supported metal or metal oxide catalysts has been rarely reported [53–58]. For example, Chou and co-workers loaded NiO onto mesoporous $\text{MgO-Al}_2\text{O}_3$ [56] and $\text{CaO-Al}_2\text{O}_3$ [57], and reduced the catalysts in H_2 . The obtained supported Ni catalysts showed good performance for the CO_2 reforming of CH_4 . Because MO_x incorporated into the mesoporous framework may influence the catalytic performance of supported metal or metal oxide catalysts, it would be desirable to synthesize this kind of multi-component catalyst to obtain tunable catalytic performance.

Herein, a series of mesoporous $\text{MO}_x\text{-Al}_2\text{O}_3$ ($\text{M} = \text{Mn, Fe, Co, Ni, Cu, Ba}$) materials were prepared by a one-pot EISA method. The selected MO_x additives were chosen because they are either active components or promoters of heterogeneous catalysts useful for many reactions. Rh_2O_3 nanoparticles were then loaded onto the mesoporous mixed-oxide supports via wet impregnation (Scheme 1). The resulting catalysts were characterized by N_2 adsorption-desorption measurements, X-ray diffraction (XRD), transmission electron microscopy (TEM), inductively coupled plasma optical emission spectrometry (ICP-OES), and X-ray photoelectron spectroscopy (XPS), and their catalytic performance for CO oxidation and N_2O decom-

position was studied.

2. Experimental

2.1. Chemical reagents

The triblock copolymer Pluronic P123 (MW = 5800) was purchased from Sigma-Aldrich. Aluminum isopropoxide, 50% $\text{Mn}(\text{NO}_3)_2$ solution, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Ba}(\text{NO}_3)_2$, ethanol, and HNO_3 (67 wt%) were purchased from Sinopharm Chemical Reagent.

2.2. One-pot synthesis of mesoporous $\text{MO}_x\text{-Al}_2\text{O}_3$

Mesoporous $\text{MO}_x\text{-Al}_2\text{O}_3$ materials were prepared according to a previous EISA method [14]. In a typical synthesis, 4.0 g of P123 was dissolved in 80 mL of ethanol at room temperature. Next, 6.4 mL of 67 wt% nitric acid, 36 mmol of aluminum isopropoxide, and 4 mmol of metal nitrate were added. The mixed solution was stirred for 5 h and then dried at 60 °C for 48 h. The final gel was heated in air in a muffle oven to 700 °C at a ramp rate of 2 °C/min, and calcined at 700 °C for 4 h. The obtained sample was denoted as M-MA, where M represents Mn, Fe, Co, Ni, Cu, or Ba, and MA is an abbreviation for “mesoporous Al_2O_3 ”. The actual M content of each sample was determined by ICP-MS. Mesoporous Al_2O_3 (denoted as MA) was prepared in a similar way, except that no metal nitrate was added.

Rh/MA and $\text{Rh}/\text{M-MA}$ catalysts were prepared by wet impregnation. A 2 mL $\text{Rh}(\text{NO}_3)_3$ solution (0.01 g/mL based on Rh) was placed in an agate mortar containing 1.98 g M-MA. The mixture was ground until dry under an infrared lamp. The obtained powders were heated in a muffle oven to 500 °C at a ramp rate of 10 °C/min, and calcined at 500 °C for 3 h. The Rh in Rh/MA and $\text{Rh}/\text{M-MA}$ represents the decomposition product (i.e., Rh_2O_3) of $\text{Rh}(\text{NO}_3)_3$. The actual Rh content of the seven samples was measured by ICP-MS.

2.3. Characterization

Wide-angle powder XRD measurements were performed on an MSAL XD2 instrument with $\text{Cu K}\alpha$ radiation from $2\theta = 10.0^\circ$

Scheme 1. Schematic illustration for the preparation of the $\text{Rh}_2\text{O}_3/\text{mesoporous MO}_x\text{-Al}_2\text{O}_3$ catalysts.

to 80.0°. The scanning rate was 4°/min, and the step length was 0.01°. Small-angle X-ray scattering (SAXS) data were recorded on a NanoStar U SAXS System from $2\theta = 0.2^\circ$ to 2.8° .

N₂ adsorption-desorption isotherms were obtained using a Micromeritics Tristar 3000 instrument. Before the measurement, the sample (0.1–0.2 g) was degassed in vacuum at 300 °C for 3 h. The specific surface areas of the samples were calculated from the N₂ adsorption-desorption data using the BET method.

ICP-OES analysis was performed on a PerkinElmer OPTIMA 2100 DV optical emission spectrometer. A 50-mg sample was dissolved in a mixture of 9 mL HCl, 3 mL HNO₃, 1 mL HClO₄, 0.5 mL H₂O₂, and 3 mL HF reagents, and heated at 150 °C for 2–3 h. After that, 3 mL HCl, 1 mL HNO₃, 1 mL HF, and 0.5 mL HClO₄ were added again, and the mixture was transferred to an autoclave, heated at 180 °C for 4 h, allowed to cool, and then diluted with distilled water for analysis.

TEM images were obtained using a JEM-2011F transmission electron microscope operated at 200 kV. The catalyst samples were dispersed in ethanol by sonication, and a few drops were dropped onto a carbon-coated copper grid followed by evaporation of the solvent. The size of the Rh₂O₃ nanoparticles was obtained by measuring 100 particles for each sample using the DigitalMicrograph software.

XPS spectra were recorded on a PerkinElmer PHI 5000 C spectrometer with a Mg K α X-ray source. The binding energy was calibrated using the C 1s peak at 284.4 eV as a reference, and the deconvolution and fitting of peaks were conducted using the Peak-fit software.

Cu LMN Auger spectra were recorded using an RBD updated PHI-5000C ESCA instrument (PerkinElmer) operated at 14.0 kV with Mg K α radiation and a detection angle of 54°.

2.4. Catalytic testing

The catalytic activity of the Rh/M-MA and Rh/MA catalysts for CO oxidation and N₂O decomposition was measured in a fixed reactor. The catalyst (0.25 g) was loaded into a U-shaped glass tube for the reaction.

For CO oxidation, the reaction gas was composed of 1% CO in air. The flow rate was 50 mL/min. The catalyst was maintained at room temperature for 1 h, and heated to 200 °C at a ramp rate of 0.5 °C/min. The effluent gas was analyzed periodically (every 10 min) using an on-line gas chromatograph (GC; Agilent 7890A, equipped with a TCD detector) capable of separating CO, CO₂, N₂, and O₂, using He as a carrier gas. The CO conversion was calculated as $[(CO)_{in} - (CO)_{out}] / (CO)_{in} \times 100\%$, where $(CO)_{in}$ is the CO concentration at room temperature (at which no reaction occurs), and $(CO)_{out}$ is the CO concentration at elevated temperature. For comparison, mesoporous MO_x-Al₂O₃ and Al₂O₃ supports were tested under similar conditions, except that they were heated to 300 °C.

For N₂O decomposition, the reaction gas contained 0.5% N₂O balanced with He, and the flow rate was 60 mL/min. The catalyst was maintained at room temperature for 1 h, and the reaction temperature was then increased in steps and kept at each temperature step for 0.5 h. The effluent gas was analyzed

periodically (every 10 min) using an on-line GC (Agilent 7890A) capable of separating N₂O, N₂, and O₂. The N₂O conversion was calculated as $[(N_2O)_{in} - (N_2O)_{out}] / (N_2O)_{in} \times 100\%$.

3. Results and discussion

3.1. Characterization of supported catalysts

Fig. 1 shows the wide-angle XRD patterns of the various catalysts. The XRD pattern of Rh/MA displayed three main reflections at $2\theta = 37.5^\circ$, 45.8° , and 66.9° , which corresponded to the γ -Al₂O₃ phase (PDF#10-0425). The Rh/M-MA (M = Mn, Fe, Ni, Cu) samples did not exhibit XRD peaks corresponding to crystalline MO_x. In contrast, Rh/Co-MA showed additional peaks assignable to CoAl₂O₄, and Rh/Ba-MA showed some peaks corresponding to BaCO₃, probably caused by the reaction of BaO with CO₂ generated by the combustion of residual organic species (isopropanol and P123). For all these catalysts, no peaks from Rh₂O₃ could be detected, indicating that the Rh₂O₃ particles were highly dispersed on the supports.

Fig. 2 shows the small-angle X-scattering (SAXS) patterns of the samples. Rh/MA exhibited a very intense (100) peak around $2\theta = 0.8^\circ$ and a weak (110) peak around $2\theta = 1.0^\circ$, indicating its hexagonal mesoporous structure [34]. The observed signals from this sample were very strong, so the raw data were divided by 1000 to enable the SAXS patterns of all the samples to be depicted in one figure. In the cases of the Rh/M-MA (M = Mn, Fe, Ni, Cu) samples, the (100) peak was broader and the (110) peak disappeared completely, which indicated a partial loss of the ordered mesoporous structure. In the cases of Rh/Co-MA and Rh/Ba-MA, the (100) peak was weaker.

Table 1 shows the actual contents of Rh and the metal elements in the samples, as determined by ICP-OES. Because Rh₂O₃ is extremely difficult to dissolve in aqua regia for ICP-OES analysis, the samples were treated under harsh conditions, as described in the Experimental section. The actual Rh contents of Rh/MA and Rh/M-MA (M = Mn, Fe, Co, Ni, Cu, Ba)

Fig. 1. Wide-angle XRD patterns of Rh/MA and Rh/M-MA samples.

Fig. 2. Small-angle X-ray scattering (SAXS) patterns of Rh/MA and Rh/M-MA samples.

were determined to be 0.99 wt%, 0.87 wt%, 0.86 wt%, 0.90 wt%, 0.97 wt%, 0.92 wt%, and 0.90 wt%, respectively, equivalent to or slightly lower than the theoretical value of 1.0 wt%. The actual contents of metal elements (Mn, Fe, Co, Ni, Cu, Ba) in the samples were 8.0 wt%, 8.5 wt%, 9.2 wt%, 9.5 wt%, 11.4 wt%, and 16.2 wt%, respectively, slightly lower than the theoretical values of 10.1 wt%, 10.4 wt%, 11.0 wt%, 11.0 wt%, 11.7 wt%, and 19.8 wt%, respectively. Note that the M/Al molar ratio of the starting materials used to synthesize of $\text{MO}_x\text{-Al}_2\text{O}_3$ was 1/9.

Fig. 3 shows the N_2 adsorption-desorption isotherms and pore size distributions of the catalysts. The corresponding textural properties (BET surface area, pore volume, and pore size) are listed in Table 1. The isotherms presented typical type IV curves with H1 shaped hysteresis, characteristic of mesoporous materials. The pore size distributions of Rh/M-MA catalysts were in the range of 2.5–9.5 nm.

Table 1
Textural properties and composition of various catalysts.

Catalyst	Rh content (wt%)	M content (wt%)	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
Rh/MA	0.99	—	259	0.54	4.28
Rh/Mn-MA	0.87	8.0	289	0.64	4.37
Rh/Fe-MA	0.86	8.5	222	0.54	4.70
Rh/Co-MA	0.90	9.2	243	0.54	4.41
Rh/Ni-MA	0.97	9.5	297	0.66	4.50
Rh/Cu-MA	0.92	11.4	212	0.47	4.33
Rh/Ba-MA	0.90	16.2	221	0.44	4.44

Fig. 4. TEM images of Rh/MA (a), Rh/Mn-MA (b), Rh/Fe-MA (c), and Rh/Co-MA (d).

The BET surface area and pore volume of the Rh/M-MA (M = Fe, Co, Cu, Ba) catalysts were slightly lower than those of Rh/MA. In contrast, the specific surface areas of Rh/Mn-MA and Rh/Ni-MA were significantly increased. It has been reported that the nickel precursors used in the preparation of ordered mesoporous Ni-V-Al can act as swelling agents and increase the micelle size of triblock copolymers [59]. The manganese precursor may have the same effect in this work.

TEM was used to observe the morphology of the catalysts. Rh/MA exhibited uniform and hexagonal ordered mesopores, as shown in Fig. 4(a). Rh/Ni-MA showed relatively ordered

Fig. 3. N_2 adsorption-desorption isotherms and pore size distribution profiles of Rh/MA and Rh/M-MA catalysts.

Fig. 5. TEM images of Rh/Ni-MA (a), Rh/Cu-MA (b), and Rh/Ba-MA (c), and HRTEM image of Rh/Ba-MA (d).

mesopores (Fig. 5(a)), and Rh/Mn-MA (Fig. 4(b)), Rh/Fe-MA (Fig. 4(c)), Rh/Co-MA (Fig. 4(d)), and Rh/Cu-MA (Fig. 5(b)) showed worm-like nanopores. In contrast, Rh/Ba-MA did not have many ordered mesoporous and some BaCO_3 aggregates were observed in Fig. 5(c). Fig. 5(d) shows that the lattice spacing of the Rh/Ba-MA sample was 0.379 nm, consistent with the lattice spacing of (111) planes of BaCO_3 .

Fig. 6 and Fig. 7 show the HRTEM images of the catalysts, highlighting the sizes and distribution of Rh_2O_3 nanoparticles on the supports. It can be seen that the Rh_2O_3 nanoparticles were located inside the pores. More importantly, the dispersion of the nanoparticles was very good and no large particles were found on any of the catalysts. The average sizes of the Rh_2O_3 nanoparticles on the MA and M-MA ($M = \text{Mn, Fe, Co, Ni, Cu, Ba}$) supports were 1.2 ± 0.3 , 1.0 ± 0.3 , 1.0 ± 0.2 , 0.9 ± 0.3 , 0.8 ± 0.3 , 1.0 ± 0.2 , and 1.2 ± 0.3 nm, respectively.

Fig. 6. HRTEM images and average particle size of Rh/MA, Rh/Mn-MA, and Rh/Ni-MA.

The Rh 3d and metal oxide XPS spectra of the samples are shown in Figs. 8 and 9, respectively. Two evident main peaks at approximately 309–309.3 eV and 313.8–314.1 eV were observed, which can be assigned to Rh^{3+} [60,61]. These results confirm that the Rh species in the supports were Rh_2O_3 .

In Fig. 9, the Mn 2p and Fe 2p XPS peaks are attributed to Mn^{4+} (MnO_2) [62,63] and Fe^{3+} (Fe_2O_3) [64]. Rh/Co-MA exhibited two features assignable to Co^{2+} , a main peak at 781.3 eV and a Co^{2+} satellite located at 785.8 eV [65,66]. The Co^{2+} species in Rh/Co-MA may have been CoAl_2O_4 . This was not only confirmed by the XPS and XRD data, but also confirmed by the blue color of the sample because CoAl_2O_4 is blue [67]. Rh/Ni-MA exhibited a Ni 2p_{3/2} main peak at 855.8 eV with a satellite peak at around 862.0 eV, characteristic of NiAl_2O_4 [39,59]. Note that the binding energy of pure NiO should be 853.6 eV [36,37]. Therefore, the Ni species in Rh/Ni-MA was NiAl_2O_4 [39,59]. Rh/Cu-MA showed two Cu 2p_{3/2} peaks at 934.1 and 932.3 eV, with a satellite near 938.5–946.6 eV. The peak at 932.3 eV can be assigned to Cu^+ [68], and the peak at 934.1 eV corresponds to Cu^{2+} [68] in CuO. The ratio of $\text{Cu}^+ / (\text{Cu}^+ + \text{Cu}^{2+})$ was 11.45%. Because the Cu 2p_{3/2} signals of Cu^+ and Cu^0 can hardly be differentiated, a Cu LMM Auger spectrum was recorded. The broad peak was deconvoluted into a main peak at 917.2 eV (Cu^{2+}) and a minor peak at 913.4 eV (Cu^+) [69]. Finally, the peaks observed in the Ba 3d XPS spectrum of Rh/Ba-MA were attributed to Ba^{2+} (BaO/BaCO_3) [70], which means that Ba^{2+} existed in the form of BaO and/or BaCO_3 in the sample.

Fig. 7. HRTEM pictures and average particle sizes of Rh/M-MA ($M = \text{Fe, Co, Cu, Ba}$).

Fig. 8. Rh 3d XPS spectra of Rh/M-MA.

Fig. 9. Metal species XPS spectra of Rh/M-MA.

3.2. Catalytic CO oxidation and N₂O decomposition

The elimination of CO is useful in pollution control, H₂ fuel cells, and many other applications. Fig. 10 presents the CO oxidation reactivity over the Rh/MA and Rh/M-MA catalysts. Rh/Mn-MA showed the best activity among the samples, and 100% CO conversion was obtained at 145 °C. The catalytic activity (evaluated from T_{50} values) of the catalysts followed the sequence Rh/Mn-MA (122 °C) > Rh/Fe-MA (130 °C) $\approx$ Rh/Cu-MA (131 °C) > Rh/Co-MA (136 °C) > Rh/Ni-MA (156 °C) > Rh/MA (161 °C) > Rh/Ba-MA (171 °C). It should be men-

tioned that the supported Rh catalysts were tested in CO oxidation up to 200 °C, and all of them reached 100% CO conversion below 200 °C. In our control experiments, the MO_x-Al₂O₃ supports were tested in CO oxidation up to 300 °C. As shown in Fig. 11, the activity followed the sequence Cu-MA > Mn-MA > Fe-MA > Co-MA > Ba-MA > MA > Ni-MA. Most of the supports were not very active below 200 °C.

These results mean that although the M-MA supports may show some activity for CO oxidation at or above 200 °C, when Rh₂O₃ nanoparticles are loaded onto these supports, the main active species for CO oxidation below 200 °C is Rh₂O₃ but not

Fig. 10. CO oxidation reactivity over Rh/MA and Rh/M-MA catalysts.

Fig. 11. CO oxidation reactivity over MA and M-MA supports.

M-MA. Thus, the role of the MO_x ($M = \text{Mn, Fe, Co, Ni, Cu}$, not including Ba) additive is to promote the Rh_2O_3 species. The reason for this promotional effect is not clear at this stage, but structural effects can be excluded because the Rh/M-MA samples were less ordered than Rh/MA. The promotional effect was also not caused by a difference in the size of the Rh_2O_3 nanoparticles on different supports, because the average particle sizes were similar. Further research is still needed to understand the observed promotional effect of the MO_x additives.

N_2O has been identified as a greenhouse gas, and therefore its elimination is very important for the environment. Fig. 12 shows the results of N_2O conversion over the Rh/MA and Rh/M-MA catalysts as a function of reaction temperature. The catalytic activity (evaluated from their T_{50} values) of the Rh/M-MA catalysts followed the sequence Rh/Co-MA (283°C) > Rh/Ni-MA (287°C) $\approx$ Rh/Fe-MA (290°C) $\approx$ Rh/Ba-MA (292°C) > Rh/MA (301°C) > Rh/Cu-MA (314°C) > Rh/Mn-MA (321°C). In our control experiments, the corresponding M-MA supports showed no activity for N_2O decomposition (data not shown), thus highlighting the importance of the supported Rh_2O_3 nanoparticles in this reaction.

The Rh/M-MA ($M = \text{Fe, Co, Ni, Ba}$) catalysts were more active for the N_2O decomposition, than Rh/MA, while Rh/Cu-MA and Rh/Mn-MA were less active. However, Rh/Cu-MA and Rh/Mn-MA were more active than Rh/MA for CO oxidation, i.e., the activity trend observed in the N_2O decomposition experiments was roughly the reverse of the trend seen in CO oxidation. This may be because N_2O decomposition requires the desorption of O_2 to complete the catalytic cycle, whereas CO oxidation requires the adsorption of O_2 [71].

Fig. 13 and Fig. 14 show the stability of selected catalysts as a function of reaction on stream. Different reaction temperatures were chosen to make sure that the conversions of CO or N_2O on the catalysts were high but not 100%. As shown in Fig. 13, Rh/MA, Rh/Mn-MA, and Rh/Cu-MA attained significant CO conversions at 165, 135, and 145 $^\circ\text{C}$, respectively. The initial CO conversions were similar to those observed from the conversion curves in Fig. 10. However, the catalysts became deactivated over time, especially during the initial 10 h on stream. The cat-

Fig. 13. CO oxidation stabilities over Rh/MA and Rh/M-MA ($M = \text{Mn, Cu}$) catalysts at different temperatures.

alytic activity of each of the samples seemed to be stabilized during the later stage of the reaction, meaning that in practical applications, complete CO conversion can still be achieved if more catalyst is put into the reactor or the reaction temperature is higher. As shown in Fig. 14, Rh/MA, Rh/Co-MA, and Rh/Ni-MA showed significant N_2O conversions at 300, 275, and 300 $^\circ\text{C}$, respectively. The initial N_2O conversions were similar to those observed in the conversion curves in Fig. 12. The N_2O conversions then increased over time and became stable during the later stage of the reaction.

To put the current work in perspective, the activity of the most active Rh/Co-MA obtained in this study was compared with those of other Rh catalysts for CO oxidation and N_2O decomposition reported in the literature. Because the catalyst amount, Rh content, CO (N_2O) concentration, and flow rate used differ between studies, specific rates over the different catalysts at the same temperature were calculated. As shown in Table 2, Rh/Mn-MA showed a specific rate of $597 \text{ mmol g}_{\text{Rh}}^{-1} \text{ h}^{-1}$ in CO oxidation at 140 $^\circ\text{C}$, higher than those of Rh/MA ($97 \text{ mmol g}_{\text{Rh}}^{-1} \text{ h}^{-1}$ in this study and Rh/ Al_2O_3 ($0 \text{ mmol g}_{\text{Rh}}^{-1} \text{ h}^{-1}$).

Fig. 12. N_2O conversion over Rh/MA and Rh/M-MA ($M = \text{Mn, Fe, Co, Ni, Cu, Ba}$) catalysts.

Fig. 14. N_2O decomposition stabilities over Rh/MA and Rh/M-MA ($M = \text{Co, Ni}$) catalysts at different temperatures.

Table 2

Comparison of the catalytic performance of various Rh-based catalysts in CO oxidation.

Catalyst	Catalyst amount (g)	Rh loading (wt%)	CO concentration (vol%)	Flow rate (mL/min)	CO conversion at 140 °C (%)	Specific rate at 140 °C (mmol g _{Rh} ⁻¹ h ⁻¹)	Ref.
Rh/Mn-MA	0.25	0.87	1	50	97	597	this work
Rh/MA	0.25	0.99	1	50	18	97	this work
Rh/γ-Al ₂ O ₃	1.0	0.36	0.1	110	0	0	[72]
Rh/CeO ₂	0.1	2.50	0.1	100	100	> 107	[73]
Rh/AlPO ₄	0.25	1.50	1	50	64	228	our data
Rh/ZnPO ₄	0.25	3.02	1	50	100	177	our data
Rh/HAP	0.25	2.99	1	50	100	> 179	our data

Table 3Comparison of the catalytic performance of various Rh-based catalysts in N₂O decomposition.

Catalyst	Catalyst amount (g)	Rh loading (wt%)	N ₂ O concentration (vol%)	Flow rate (mL/min)	N ₂ O conversion at 325 °C (%)	Specific rate at 325 °C (mmol g _{Rh} ⁻¹ h ⁻¹)	Ref.
Rh/Co-MA	0.25	0.90	0.5	60	97	346	this work
Rh/MA	0.25	0.99	0.5	60	86	279	this work
Rh/γ-Al ₂ O ₃	0.1	0.50	0.1	100	36	192	[74]
Rh/Fe-SBA-15	0.1	0.62	0.5	40	0	0	[75]
Rh/Cu-SBA-15	0.1	0.67	0.5	40	1	8	[75]
Rh/KIT-6	0.05	1.00	0.17	100	0	0	[76]
Rh/CeO ₂	0.05	0.50	0.1	100	100	> 1071	[77]
Rh/LaPO ₄	0.5	2.69	0.5	60	42	25	[78]
Rh/HAP	0.5	0.58	0.5	60	100	> 277	[78]

reported in the literature [72]. Rh/Mn-MA was also more active than our previous Rh/AlPO₄ (228 mmol g_{Rh}⁻¹ h⁻¹) and Rh/ZnPO₄ (177 mmol g_{Rh}⁻¹ h⁻¹) catalysts. However, it is difficult to compare Rh/Mn-MA with Rh/CeO₂ (> 107 mmol g_{Rh}⁻¹ h⁻¹) [73] or Rh/hydroxyapatite (> 179 mmol g_{Rh}⁻¹ h⁻¹) because the latter two catalysts showed 100% CO conversion below 140 °C.

As shown in Table 3, Rh/Co-MA exhibited a specific rate of 346 mmol g_{Rh}⁻¹ h⁻¹ in N₂O decomposition at 325 °C, making it apparently more active than Rh/MA (279 mmol g_{Rh}⁻¹ h⁻¹), Rh/Al₂O₃ (192 mmol g_{Rh}⁻¹ h⁻¹) [74], Rh/Fe-SBA-15 (0 mmol g_{Rh}⁻¹ h⁻¹) [75], Rh/Cu-SBA-15 (8 mmol g_{Rh}⁻¹ h⁻¹) [75], and Rh/KIT-6 (0 mmol g_{Rh}⁻¹ h⁻¹) [76], but less active than Rh/CeO₂ (> 1071 mmol g_{Rh}⁻¹ h⁻¹) [77]. Rh/Co-MA was more active than Rh/LaPO₄ (25 mmol g_{Rh}⁻¹ h⁻¹), but it is difficult to compare Rh/Co-MA with Rh/hydroxyapatite (> 277 mmol g_{Rh}⁻¹ h⁻¹) because the latter catalyst showed 100% N₂O conversion below 325 °C [78].

4. Conclusions

A series of mesoporous MO_x-Al₂O₃ (M = Mn, Fe, Co, Ni, Cu, Ba) materials were prepared via a one-pot synthetic method. The obtained materials were used as supports for the loading of Rh₂O₃. The oxides of Mn, Fe, Ni, and Cu were highly dispersed in the mesoporous matrix, whereas those of Co and Ni reacted with MA to form CoAl₂O₄ and NiAl₂O₄ spinels, and some BaCO₃ formed on MA for Rh/Ba-MA. All the obtained catalysts had high specific surface area, large pore volume, and nanopores. Rh₂O₃ particles of around 1 nm in size were well dispersed on the supports. All of these factors caused the mesoporous catalysts to exhibit excellent catalytic activity. For CO oxidation, the activity of the catalysts followed the sequence Rh/Mn-MA >

Rh/Fe-MA ≈ Rh/Cu-MA > Rh/Co-MA > Rh/Ni-MA > Rh/MA > Rh/Ba-MA. For N₂O decomposition, the activity followed the sequence Rh/Co-MA > Rh/Ni-MA ≈ Rh/Fe-MA ≈ Rh/Ba-MA > Rh/MA > Rh/Cu-MA > Rh/Mn-MA. Although the reasons for the differences in activity between the different catalysts are not yet explicitly clear, we have successfully demonstrated the application of mesoporous MO_x-Al₂O₃ as a support for Rh₂O₃ catalysts. Although here we chose CO oxidation and N₂O decomposition as probe reactions to compare the catalytic activity of the samples, we believe that these catalysts may be useful for other reactions, considering the broad usefulness of Rh₂O₃ and Al₂O₃ in catalysis.

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Graphical Abstract

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Rh₂O₃/mesoporous MO_x-Al₂O₃ (M = Mn, Fe, Co, Ni, Cu, Ba) catalysts: Synthesis, characterization, and catalytic applications

Huan Liu, Yi Lin, Zhen Ma*
Fudan University

Mesoporous MO_x-Al₂O₃ (M = Mn, Fe, Co, Ni, Cu, Ba) materials were prepared by a one-pot evaporation-induced self-assembly method. Rh₂O₃ nanoparticles were loaded onto these mesoporous supports via wet impregnation.

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Rh₂O₃/介孔MO_x-Al₂O₃ (M = Mn, Fe, Co, Ni, Cu, Ba)催化剂: 合成、表征和催化应用

刘欢, 林毅, 马臻*

复旦大学环境科学与工程系, 上海市大气颗粒物污染与防治重点实验室, 上海200433

摘要: 近年来, 研究者们开发了自组装合成介孔氧化铝的方法, 并以介孔氧化铝为载体负载金属氧化物, 还尝试合成介孔MO_x-Al₂O₃复合氧化物。但以介孔MO_x-Al₂O₃复合氧化物为载体负载金属氧化物, 并将这类材料用于催化中的例子相对较少。本工作以非离子型三嵌段共聚物(P123)为模板剂, 异丙醇铝为氧化铝前驱物, 采用一锅法快速制备了有序介孔Al₂O₃(MA)及一系列MO_x-Al₂O₃ (M = Mn, Fe, Co, Ni, Cu, Ba)材料, 并以这些材料为载体采用浸渍法制备了Rh/MA和Rh/M-MA催化剂。采用N₂吸附-脱附、X射线粉末衍射、透射电镜、X射线光电子能谱及电感耦合等离子体发射光谱等对催化剂结构和性质进行了表征, 考察了催化剂对CO氧化和N₂O分解的催化活性和稳定性。

结果表明, 一锅法制备的各催化剂均有大的比表面积、大的孔容和均一的孔径。Rh/Mn-MA和Rh/Fe-MA中掺杂金属氧化物分别为MnO₂和Fe₂O₃, 在Rh/Co-MA和Rh/Ni-MA上, Co和Ni分别与介孔氧化铝形成了NiAl₂O₄尖晶石结构; Rh/Cu-MA上还有CuO和少量Cu⁺; 对于Rh/Ba-MA催化剂, 其载体的介孔有序性被破坏并有BaCO₃生成。在所有催化剂上, 负载的Rh₂O₃颗粒高度分散, 其颗粒尺寸分布在1 nm左右。对于CO氧化, 催化剂的T₅₀ (CO转化率到达50%的温度)活性顺序为: Rh/Mn-MA (122 °C) > Rh/Fe-MA (130 °C) ≈ Rh/Cu-MA (131 °C) > Rh/Co-MA (136 °C) > Rh/Ni-MA (156 °C) > Rh/MA (161 °C) > Rh/Ba-MA (171 °C)。大多数载体在200 °C以下没有活性。对于N₂O分解, 催化剂的T₅₀ (N₂O转化率到达50%的温度)活性顺序为: Rh/Co-MA (283 °C) > Rh/Ni-MA (287 °C) ≈ Rh/Fe-MA (290 °C) ≈ Rh/Ba-MA (292 °C) > Rh/MA (301 °C) > Rh/Cu-MA (314 °C) > Rh/Mn-MA (321 °C)。这些载体在400 °C以下都没有活性。

实验证明, 通过掺杂的方法可以调变介孔Al₂O₃的物理化学性质, 负载Rh₂O₃后, 催化性能进一步被调变。虽然本文仅选取CO氧化和N₂O分解作为探针反应来比较这一类介孔氧化物材料的催化活性, 考虑到Rh₂O₃和Al₂O₃在催化中的广泛使用, 我们认为这些催化剂有可能用在其他反应中。

关键词: 一锅法; 介孔氧化铝; 金属氧化物; CO氧化; N₂O分解

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*通讯联系人. 电话: (021)65642997; 传真: (021)65643597; 电子邮箱: zhenma@fudan.edu.cn

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