Short communication

Comparison between unsupported mesoporous Co_3O_4 and supported Co_3O_4 on mesoporous silica as catalysts for N_2O decomposition

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ABSTRACT

Mesoporous Co_3O_4 (meso-Co_3O_4) and Co_3O_4 nanoparticles supported on mesoporous silica SBA-15 (Co/SBA-15) were prepared by hydrothermal synthesis and an impregnation method, respectively. Although the as-prepared meso-Co_3O_4 had mesopores and a higher surface area comparable to that of Co/SBA-15, its catalytic activity for N_2O decomposition was much lower than that of Co_3O_4/SBA-15. The low catalytic activity of meso-Co_3O_4 mainly stems from the drastic decrease of the meso-Co_3O_4 surface area under the reaction condition used. On the other hand, Co/SBA-15 maintained its high surface area and mesopores with the aid of a robust silica support. This finding indicates that Co_3O_4 supported by a support is much more stable and efficient than meso-Co_3O_4 under N_2O decomposition reaction conditions.

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1. Introduction

Nitrous oxide (N_2O) is not only one of most harmful substances related to ozone-depletion in the stratosphere but also the third most influential greenhouse gas. [1–4] There are many remediation technologies to reduce N_2O emissions, such as thermal decomposition [5,6], catalytic reduction [7–10], and catalytic decomposition [11–20]. Among them, catalytic decomposition appears to be the most promising technique because it requires simpler facilities and less energy compared to other techniques [21]. To take advantage of the catalytic decomposition technique, the catalyst plays a very important role. Zeolites [14], noble metals supported on alumina or silica [15–17], and metal oxides [18–20] have been used as catalysts for this purpose.

Transition-metal oxides have attracted much attention. Among them, Co_3O_4-based catalysts show high activity for N_2O decomposition [18,19,22–25]. To enhance this level of activity with a high surface area and mesopores, mesoporous Co_3O_4 was prepared by a hard template synthesis method. Although mesoporous Co_3O_4 showed higher catalytic activity for N_2O decomposition in a recent report [26,27], hard template synthesis using mesoporous silica is complex and expensive because it involves at least three major steps (template preparation, the incorporation of Co_3O_4, and the removal of the template). Moreover, the expensive mesoporous silica hard template must be sacrificed. Considering these drawbacks, the preparation of mesoporous Co_3O_4 by hard template synthesis is not suitable for the commercialization of transition metal oxide catalysts.

To find a solution to this problem, two types of Co_3O_4 catalysts were prepared. The first is mesoporous Co_3O_4 prepared by soft template synthesis, as soft template synthesis is an easier and more facile method than hard template synthesis. The second is Co_3O_4 nanoparticles supported on mesoporous silica SBA-15 by impregnation. Once this type of supported catalyst is optimized, it can easily be utilized for the preparation of a pellet type catalyst, an essential step for commercialization. These two types of catalysts were characterized by N_2 adsorption, XRD, TEM to assess the surface areas, and according to the Co_3O_4 particle sizes and shapes. The catalytic activities of these catalysts were explained in terms of the physical properties of the corresponding catalysts: mesoporous Co_3O_4 vs. Co_3O_4 nanoparticles supported on mesoporous silica.

2. Experimental section

2.1. Preparation of mesoporous Co_3O_4

All chemicals were used as received. Mesoporous Co_3O_4 was synthesized by dissolving 0.08 mol $Co(NO_3)_2 \cdot 6H_2O$ in 100 ml ethylene glycol (EG) while stirring at room temperature for 3 h. After stirring, the solution was put into a Teflon-lined stainless steel autoclave. Hydrothermal reactions were carried out at 150 °C for 10 h. After cooling to room temperature, the precipitates were centrifuged, and washed with deionized water. This was followed by drying at 100 °C for 12 h. This sample was designated as the "as-prepared meso-Co_3O_4."

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2.2. Preparation of Co_3O_4 nanoparticles supported on SBA-15

SBA-15, a silica support with ordered mesopores, was synthesized according to a process reported in the literature [28]. The typical synthesis procedure was as follows. Pluronic P-123 (average M_n ~ 5800, Aldrich) with a weight of 8.0 g was dissolved in 320 g of 2 M HCl and 60 g of deionized water. After 17 g of tetraethylorthosilicate (37 wt.%, Aldrich) was added, this reaction mixture was vigorously stirred for 5 min. It was then kept at 35 °C for 24 h, after which it was heated to 100 °C for 20 h under a static condition. The resulting white powder was filtered without washing and then dried at 100 °C overnight. The obtained powder was calcined at 550 °C for 3 h.

During the preparation of Co_3O_4 nanoparticles supported on SBA-15 (Co/SBA-15), Co/SBA-15 catalysts with different cobalt loading levels (16.9, 23.4, 30.0 wt.%) were prepared by an incipient wetness method. For the typical preparation of 30.0 wt.% Co/SBA-15, 14.11 g of $Co(NO_3)_2 \cdot 6H_2O$ was dissolved in 10.0 g of DI water. In the incipient wetness method, one third of this solution was added drop-wisely onto 7.0 g of SBA-15 and then dried at 120 °C for 4 h. This cycle was repeated twice more. The resultant powder was calcined in air at 550 °C for 4 h. To investigate the calcination temperature, the calcination temperatures used were 700 °C and 850 °C.

2.3. Characterization of the catalysts

The structures of cobalt oxides (mesoporous Co_3O_4 and Co_3O_4 supported on SBA-15) were investigated by X-ray diffraction (XRD; X'pert Pro Multi-purpose, Cu, $K\alpha$) and by high-resolution transmission electron microscopy (HR-TEM; Philips Tecnai F20). Nitrogen adsorption-desorption isotherms were measured at 77 K using a Micromeritics ASAP2020 instrument. The surface areas were calculated according to the Brunauer-Emmett-Teller (BET) method. The pore size distribution was obtained from the desorption branch of the isotherm by means of the Barrett-Joyner-Halenda (BJH) method.

2.4. N_2O decomposition reaction conditions

For the decomposition of the N_2O reaction, a fixed-bed reactor with quartz (inner diameter = 10 mm) was used. The amount of catalyst used was 1.5 g with a particle size between 200 and 250 μm. The total volume of the catalyst was 2.66 ml. To maintain the total volume, quartz beads of the same particle size were added as a diluent. Before the reaction, all of the catalysts were activated in a N_2/O_2 mixture gas (1:1 with a total flow rate of 200 sccm) from room temperature to 550 °C for 4 h and then maintained at 550 °C for 1 h. The total flow rate of the reactant gas was 2 l/min and the concentration of N_2O in the flow was 500 ppm. The gas hourly space velocity (GHSV) was 45,100 h^{-1}. To investigate the oxygen effect, 3 vol% of O_2 was added. The change in the N_2O concentration was determined by an infrared gas analyzer (Madur Polska, Sensonic IR-1). During the reaction, temperature increased sequentially from 200, 300, 400, to 500 °C. The ramping rate was 5 °C/min and the designated temperature was maintained for 1 h to measure N_2O conversion at this temperature.

3. Results and discussion

3.1. Characterization of mesoporous Co_3O_4

Table 1 and Figure S1 show the surface area, porosity, and crystal phase of meso-Co_3O_4 before and after the N_2O decomposition reaction according to the nitrogen adsorption-desorption isotherms and XRD patterns. Figure S1(a) shows the XRD pattern of the meso-Co_3O_4 samples before and after N_2O decomposition reaction. Before the N_2O decomposition reaction, the meso-Co_3O_4 sample showed very weak peaks in the XRD pattern. The as-synthesized meso-Co_3O_4 sample appears to have amorphous or extremely small size cobalt oxide particles.

Table 1
Physical properties of mesoporous Co_3O_4 obtained by N_2 adsorption at 77 K.

Properties	As-synthesized	After reaction
BET surface area [m^2/g]	154	28
Total pore volume[a] [cm^3/g]	0.21	0.16
Average pore diameter[b] [nm]	5.5	23.3

[a] Total pore volume at $P/P_0 = 0.98$ (P: partial pressure of N_2 at 77 K, P_0: 1 atm, saturated N_2 partial pressure at 77 K).
[b] Average pore diameter was calculated with the equation $4V/A$, where V is total pore volume at $P/P_0 = 0.98$ and A is BET surface area.

After the N_2O decomposition reaction, however, the meso-Co_3O_4 sample showed sharp peaks which correspond to the spinel Co_3O_4 structure (PDF 43-1003). Judging from the full width at half maximum (FWHM) of the peaks, the crystal size of Co_3O_4 increased sharply after the reaction. The as-prepared meso-Co_3O_4 (before the reaction) showed a high BET surface area (154 m^2/g). The shape of the N_2 adsorption-desorption isotherm classified it as a type IV isotherm. The BJH pore size distribution for the meso-Co_3O_4 catalyst before the reaction shown in the inset of Figure S1(b) indicates that meso-Co_3O_4 had well-developed mesopores before the reaction and that its pore size was approximately 4 nm. After the N_2O decomposition reaction, which was carried out from 200 to 500 °C, the surface area and porosity of the meso-Co_3O_4 changed drastically. The BET surface area decreased to 28 m^2/g. This low surface area is nearly identical to that of commercially available bulk Co_3O_4. The shape of the N_2 isotherm changed to type III, indicating that the meso-Co_3O_4 lost its mesopores after the N_2O decomposition reaction. These results imply that the meso-Co_3O_4 catalyst lost its mesopores, as noted above, and became a non-porous material with a low surface area due to the agglomeration of Co_3O_4 particles during the N_2O decomposition reaction. Thus, the meso-Co_3O_4 synthesized in this study by a hydrothermal method with a soft-template at a relatively low temperature (150 °C) does not appear to be suitable as a catalyst for the N_2O decomposition reaction at higher temperatures due to the collapse of the mesopores and the agglomeration of Co_3O_4 nanoparticles.

3.2. Characterization of Co/SBA-15 catalysts

Apart from the meso-Co_3O_4, Co_3O_4 nanoparticles supported on mesoporous silica SBA-15 (Co/SBA-15) maintained their nanostructure and mesopores before and after the N_2O decomposition reaction. The maximum loading of cobalt on SBA-15 was 30.0 wt.%. To achieve 30 wt.% loading, one third of a cobalt nitrate solution [14.11 g of $Co(NO_3)_2 \cdot 6H_2O$ in 10 g H_2O] was added in a drop-wise manner onto mesoporous silica SBA-15 and then dried at 120 °C for 4 h. This cycle was repeated twice more. When the designated cobalt loading exceeded 30 wt.% (for example, 35 wt.%) the cobalt nitrate solution no longer diffused into the mesoporous silica support in the fourth cycle. This indicates that cobalt nitrate salt already occupied most of the pore volume in SBA-15.

The XRD patterns shown in Figure S2(a) indicate that the crystal structure of the cobalt species supported on SBA-15 was also spinel Co_3O_4 (PDF 43-1003). Low-angle XRD patterns of Co/SBA-15 with different Co loading levels (16.9–30.0 wt.%) are displayed in Figure S2(b). Although the intensities of the peaks related to the mesopores [(100), (110), (200)] decreased after supporting Co_3O_4, Co/SBA-15 samples with different Co loading level retain their mesopore structures. Figure S2(c) shows the nitrogen isotherms and BJH pore size distributions of the SBA-15 and Co/SBA-15 catalysts. The shapes of the N_2 adsorption-desorption isotherms for the SBA-15 support and all of the Co/SBA-15 samples with different cobalt loading levels indicated type IV shapes. The BJH pore size distributions for the Co/SBA-15 samples shown in the inset of Figure S2(c) indicate that all samples had mesopores. Table 2 also shows that the Co/SBA-15 samples had high surface areas (more than 300 m^2) and large pore volumes (more