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Simple, Low-cost Preparation of High Surface Area Co_3O_4–CeO_2 Catalysts for Total Decomposition of Toluene

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High surface area Co_3O_4–CeO_2 catalysts were prepared by the simple calcination of carbonate–precursor mixtures at 300 °C. The Co_3O_4–CeO_2 catalyst with a Co/Ce molar ratio of 1 showed high activity for toluene decomposition, comparable to that of Pt(0.08 wt %)/zeolite catalyst. The total decomposition of toluene was achieved at degradation temperatures as low as 200 °C. The Co_3O_4–CeO_2 catalyst was highly stable, even after two weeks of reaction.

Volatile organic compounds (VOCs) are significant atmospheric pollutants, due to their toxicity and/or malodorous nature. Toluene, which is widely used in the industrial world, is one such VOC. The most active catalysts for toluene degradation are based on platinum or palladium, which are dispersed on high surface area supports.[1,2] However, their wide application remains difficult due to the high cost of the noble metals. Therefore, it is important to develop low-cost catalysts, i.e., noble metal-free catalysts, such as CeO_2[3,4] and Co_3O_4.[5] In CeO_2 and Co_3O_4, Ce^{3+}/Ce^{4+} and Co^{2+}/Co^{3+} redox cycling plays an important role in the reactions.[3–5]

Recently, it was reported that strong interaction between CeO_2 and Co_3O_4 resulted in high activity for toluene decomposition. The best interaction as well as the highest performance was observed on a sample with a peculiar composition (Co/Ce atomic ratio = 1).[6] The total decomposition of toluene was observed at 275 °C on this sample, which had a surface area of $33\,m^2\,g^{-1}$.

In many cases, a high surface area would be an important factor in obtaining high catalytic activity. In the present study, we successfully prepared Co_3O_4–CeO_2 catalysts with high surface areas, of up to $147\,m^2\,g^{-1}$. The catalysts showed high activity for the total decomposition of toluene at reaction temperatures as low as 200 °C. A simple preparation method, the calcination of carbonate–precursor mixtures at a low temperature, was employed instead of the more commonly employed calcination of residue after coprecipitation. The relationship between catalytic properties and activity was investigated, and the stability of the catalyst was tested.

A series of Co_3O_4–CeO_2 catalysts with various Co/Ce molar ratios was prepared by the calcination of carbonate–precursor mixtures. An appropriate amount of $2CoCO_3\cdot 3Co(OH)_2\cdot 4H_2O$ (Kanto Chemical) was physically mixed with $Ce_2(CO_3)_3\cdot 8H_2O$ (Kanto Chemical) and then calcined in air at 300–650 °C for 5 h. These obtained materials were labeled CoCeX:Y-Z, where X:Y refers to the Co/Ce molar ratio and Z refers to the calcination temperature. As references, Co_3O_4 and CeO_2 were also prepared by calcination of the carbonate–precursors of cobalt and cerium at 300 °C for 5 h and labeled Co_3O_4-300 and CeO_2-300, respectively. These calcined samples were pelletized and then crushed and sieved to ca. 0.5-mm-size particles. For comparison, Pt(0.08 wt %)/zeolite catalyst (y-type zeolite, φ 0.5 mm) was also employed. Pt was introduced by incipient wetness impregnation using an appropriate solution of H_2PtCl_6, followed by reduction at 400 °C for 5 h under H_2 atmosphere.

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku diffractometer RINT-2100 using Cu Kα radiation (40 kV, 40 mA). Brunauer–Emmett–Teller (BET) specific surface area was measured on a BELSORP-mini II. Before the measurements, the samples were treated under N_2 flow at 200 °C for 2 h.

Reaction tests were carried out using a flow reaction system connected to a permeater standard gas generation system. The diffusion tube containing toluene(l) was placed in the permeater, which was set to 40 °C, to generate a constant amount of toluene(g). He(g) was used as the carrier gas. He containing toluene was mixed with a mixture of N_2 and O_2 ($100\,mL\,min^{-1}$), giving a total gas flow of $304\,mL\,min^{-1}$ (toluene: 210 ppm, O_2: 13%, GHSV: $16600\,h^{-1}$). The catalyst (1 g) was packed in a Pyrex reactor ($1.1\,cm^3$). When the volume of the employed catalyst was low, an appropriate amount of quartz sand was added to obtain a similar GHSV (gas hourly space velocity). The reaction was started after toluene adsorption reached equilibrium on the catalyst. The amounts of unreacted toluene and CO_2 product in the outflow gases were analyzed on line by gas chromatography (GC) with a flame ionization detector (FID) and thermal conductivity detector (TCD), respectively. In some cases, the outflow gas was also measured by proton-transfer reaction mass spectrometry (PTR-MS) to check for trace products (ppb order), which may have been undetectable by GC.

For stability testing, air ($376\,mL\,min^{-1}$) was used as an oxidant instead of an O_2 and N_2 mixture. The untreated air was supplied by a compressor, at a gas flow rate of $607\,mL\,min^{-1}$ (toluene: 230 ppm, O_2: 13%, GHSV: $33200\,h^{-1}$).

Since the catalytic total decomposition of toluene is desirable, because it avoids the generation of toxic by-products, CO_2 yield was used as a parameter to represent the catalytic activity. Figures 1a–1e shows the dependence of the CO_2 yield on the reaction temperature over Co_3O_4–CeO_2 catalyst samples having various molar ratios and bare Co_3O_4 and CeO_2. The reaction temperature for a CO_2 yield of 100% (T_{100}) on CoCe1:1-300 was much lower than on Co_3O_4-300, CeO_2-300, or other Co_3O_4–CeO_2 catalysts. The surface areas of CoCe2:1-300, CoCe1:2-300, and CoCe1:1-300 were similar, and the values were between those of CeO_2-300 and Co_3O_4-300 (Table 1, Entries 1–5). It was previously reported that a higher dispersion of Co_3O_4 on CeO_2 contributed to a higher mobility of lattice oxygen, resulting in higher performance.[6] In the present study, it was found that a Co/Ce molar ratio of 1 provided the best dispersion of Co_3O_4 on CeO_2. To study the effect of

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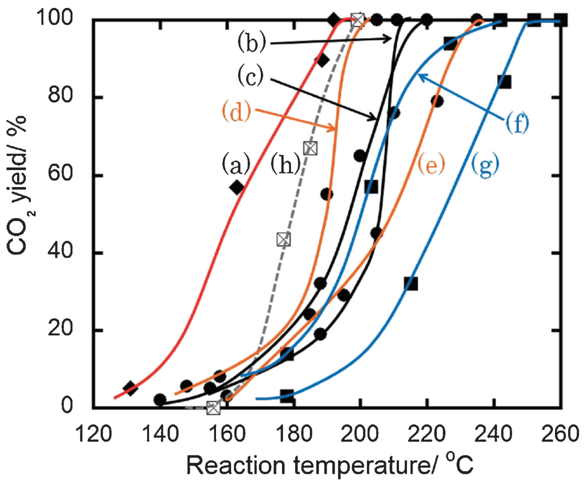

Figure 1. CO_2 yield as a function of reaction temperature over (a) CoCe1:1-300, (b) CoCe1:2-300, (c) CoCe2:1-300, (d) CeO_2-300, (e) Co_3O_4-300, (f) CoCe1:1-500, (g) CoCe1:1-650, and (h) Pt(0.08 wt %)/zeolite catalyst.

Table 1. The surface area (S_{BET}) and reaction temperature at which the CO_2 yield was 100% (T_{100}) on the samples

Entry	Sample	$S_{BET}/m^2\,g^{-1}$	$T_{100}{}^a/°C$
1	CoCe1:1-300	143	192
2	CoCe2:1-300	139	220
3	CoCe1:2-300	147	212
4	CeO_2-300	155	205
5	Co_3O_4-300	109	235
6	CoCe1:1-500	73	241
7	CoCe1:1-650	27	252
8	Pt(0.08 wt %)/zeolite	—[b]	198

[a]Reaction temperature at which CO_2 yield was 100%. [b]Not measured.

calcination temperatures on the catalytic activity of Co_3O_4–CeO_2 catalysts, CoCe1:1 samples were treated at 500 (Figure 1f) and 650 °C (Figure 1g). The samples prepared at higher calcination temperatures showed higher T_{100}. The XRD peak intensity, these peaks could be ascribed to CeO_2 and/or Co_3O_4 with no other peaks, became stronger and the shape became sharper as the calcination temperature increased (data not shown), suggesting that the particle size became larger and/or the crystallinity increased. As a result, the surface area of the catalysts decreased (Table 1, Entries 1, 6, and 7). This suggests that the crystallinity had no significant effect on the catalytic activity, but the surface area could have affected the catalytic activity. This is reasonable, because higher surface area should provide more active sites, resulting in higher catalytic activity. It is noted that the catalytic activity of CoCe1:1-300 was comparable to that of Pt(0.08 wt %)/zeolite catalyst (Figures 1a and 1h). Since T_{100} on CoCe1:1-300 was similar to that of Pt(0.08 wt %)/zeolite catalyst, it is expected that CoCe1:1-300 might replace the use of Pt-based catalysts in the future. In a separate experiment, the product gas obtained on CoCe1:1-300 was measured by PTR-MS. No VOC was detected after the reaction, either at 210 or 200 °C, and only a very small amount of toluene (0.66 ppm) and benzene (0.08 ppm) were detected when the reaction was carried out at 190 °C.

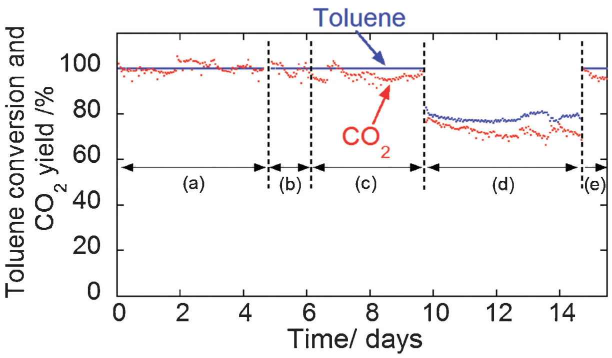

Figure 2. Stability of CoCe1:1-300 samples at various temperatures, (a) 275, (b) 264, (c, e) 245, and (d) 225 °C.

The stability of the toluene decomposition was tested after 14 days of reaction at 225–275 °C over the best sample, CoCe1:1-300, using GHSV = 33200 h^{-1}, as shown in Figure 2. Since the oxidant was untreated air, a slight periodic change of CO_2 concentration was observed due to changing CO_2 concentration in the air. The toluene conversion and the CO_2 yield were 100% at 275 and 264 °C (Figures 2a and 2b). These results demonstrated that toluene was completely decomposed to CO_2 at these reaction temperatures. The toluene conversion was 100% and the CO_2 yield was only ca. 96% at 245 °C (Figure 2c), whereas the toluene conversion was ca. 80% and the CO_2 yield was ca. 72% at 225 °C (Figure 2d). At these lower reaction temperatures, the CO_2 yields were lower than the toluene conversions. This suggests that by-products such as benzene may have been generated at these temperatures. The toluene conversion and the CO_2 yield were restored by increasing the reaction temperature to 245 °C (Figure 2e), demonstrating the high stability of the CeCo1:1-300 catalyst.

In this report, we presented a simple, low-cost method to prepare stable, highly active Co_3O_4–CeO_2 with a high surface area for the total decomposition of toluene. We expect that these findings will help enable large-scale catalytic decomposition of toluene and other VOCs in the near future.

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