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## Research Article

# Characteristics of Carbon Monoxide Oxidization in Rich Hydrogen by Mesoporous Silica with TiO<sub>2</sub> Photocatalyst

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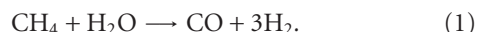
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Hydrogen (H<sub>2</sub>) is normally used as the fuel to power polymer electrolyte fuel cell (PEFC). However, the power generation performance of PEFC is harmed by the carbon monoxide (CO) in the H<sub>2</sub> that is often produced from methane (CH<sub>4</sub>). The purpose of this study is to investigate the experimental conditions in order to improve the CO oxidization performance of mesoporous silica loaded with TiO<sub>2</sub>. The impact of loading ratio of TiO<sub>2</sub> and initial concentration ratio of O<sub>2</sub> to CO on CO oxidization performance is investigated. As a result, the optimum loading ratio of TiO<sub>2</sub> and initial concentration ratio of O<sub>2</sub> to CO were 20 wt% and 4 vol%, respectively, under the experimental conditions. Under this optimum experimental condition, the CO in rich H<sub>2</sub> in the reactor can be completely eliminated from initial 12000 ppmV after UV light illumination of 72 hours.

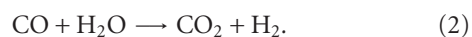
## 1. Introduction

Polymer electrolyte fuel cell (PEFC) has been developed vigorously in the world since it is an attractive and clean power generation technology. H<sub>2</sub> is normally used as the fuel to power PEFC. However, the reduction of PEFC power generation performance has been observed due to the existence of CO in the H<sub>2</sub> produced from CH<sub>4</sub>, CH<sub>3</sub>OH, and gasoline.

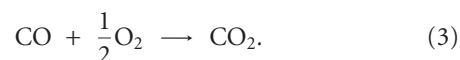
CH<sub>4</sub> is normally the feedstock to produce H<sub>2</sub> with Ni or Ru as catalyst at the high temperature range of 873 K–973 K through the following reaction:



After this reaction, there is about 10 vol% of CO in the products. The CO concentration can be reduced down to about 1 vol% by the following so-called shift reaction:



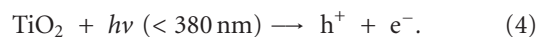
After the shift reaction, the concentration of CO needs to be further reduced down to 10 ppmV by the following selective oxidization reaction:



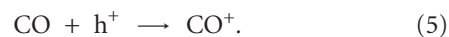
In the H<sub>2</sub> purification processes mentioned above, precious metal catalysts and thermal energy are used, and the processes are costly. An alternative process, that is, using the TiO<sub>2</sub> photocatalyst combined with adsorbent to oxidize CO is being developed recently due to its potential cost and energy saving.

TiO<sub>2</sub> can oxidize CO under illumination of ultraviolet (UV) ray (available in sunlight) through the following reaction scheme [1, 2].

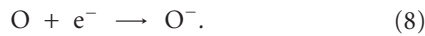
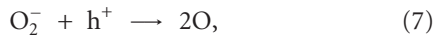
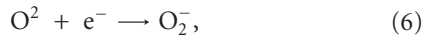
*Photocatalytic reaction:*



*Oxidization of CO:*



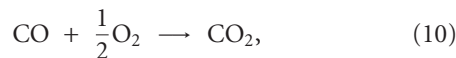
Reduction of O<sub>2</sub>:



From the products of the reactions (5) and (8), the following combined reaction occurs:



Therefore, the total reaction scheme can be written as follows:



where  $h\nu$  is the energy of UV ray.  $\text{h}^+$  and  $\text{e}^-$  represent the hole and electron produced by photocatalytic reaction, respectively.

The oxidization process with TiO<sub>2</sub> has the following merits. (1) There is a lot of TiO<sub>2</sub> reserve in the earth compared with precious metal catalyst. The amount of Ti is the 9th largest among the elements consisting the earth crust [3]. (2) Cost is lower than using precious metal catalyst. (3) Energy consumption is less and the control of the reaction process is easier since high thermal energy is not necessary. (4) Solar energy can be used for the reaction. (5) TiO<sub>2</sub> is stable in both acid and alkali environments.

Literature survey shows that TiO<sub>2</sub> photocatalyst combined with adsorbent such as activated carbon, zeolite, and silica (SiO<sub>2</sub>) was mainly used in environmental purification technologies such as NO<sub>x</sub> removal [4–6], decomposition of acetaldehyde [7], dimethylsulfide [8], 2-propanol [9], degradation of organophosphate and phosphoglycine [10], and CO<sub>2</sub> reforming into fuel like CH<sub>4</sub> and CH<sub>3</sub>OH [11, 12]. The CO oxidization by photocatalyst combined with FeO<sub>x</sub>, Al<sub>2</sub>O<sub>3</sub>, or CeO<sub>x</sub> and precious metal catalyst like Pt or Au was reported [13–15]. Furthermore, the CO oxidization characteristics of Pt loaded on zeolite without photocatalyst were also reported [16, 17]. Although there are reports on the CO oxidization characteristics of Mo/SiO<sub>2</sub> or Cr/SiO<sub>2</sub> [18, 19], there is no report on the CO oxidization characteristics of TiO<sub>2</sub> combined with adsorbent except our previous study [20]. Our previous study investigated the effect of different loading methods of TiO<sub>2</sub> to silica on CO oxidization performance. Comparing two types of TiO<sub>2</sub> particle combined with silica, that is, the silica gel particles coated with TiO<sub>2</sub> film and mesoporous silica particles loaded with TiO<sub>2</sub>, the amount of oxidized CO per unit mass of TiO<sub>2</sub> for the mesoporous silica particles loaded with TiO<sub>2</sub> was larger than that for silica gel particles coated with TiO<sub>2</sub> film. Therefore, it revealed that loading was a more effective way to make use of TiO<sub>2</sub> for CO oxidization. However, it also reported that the investigation on optimum experimental condition was necessary to promote the CO oxidization performance more.

The purpose of this study is to investigate the experimental conditions in order to improve the CO oxidization performance of mesoporous silica loaded with TiO<sub>2</sub>.

TABLE 1: Physical properties of mesoporous silica loaded with TiO<sub>2</sub>.

	Mesoporous silica loaded with TiO <sub>2</sub> particles
Particle size (mm)	0.03–0.25 (primary particle) 2.0–5.6 (agglomerated particle)
Specific surface area (m <sup>2</sup> /g)	219–1038
Average pore diameter (nm)	2.7–3.1
Pore volume (mL/g)	0.63–0.94
Ratio of loaded TiO <sub>2</sub> (wt%)	1, 10, 15, 20, 30, 60, 80

Since UV ray can penetrate the mesoporous silica, the particles of mesoporous silica loaded with TiO<sub>2</sub> can be used in a bed-type reactor. The effect of loading ratio of TiO<sub>2</sub> and initial concentration ratio of O<sub>2</sub> to CO on CO oxidization performance was investigated to decide the optimum experimental conditions. The loading ratio of TiO<sub>2</sub> is changed minutely by 1 wt%, 10 wt%, 15 wt%, 20 wt%, 30 wt%, 60 wt%, and 80 wt%. The initial concentration of O<sub>2</sub> is also changed closely by 0.5 vol%, 1 vol%, 2 vol%, 4 vol%, 6 vol%, 8 vol%, and 10 vol%. Moreover, the best CO oxidization performance of the mesoporous silica with TiO<sub>2</sub> was evaluated under the optimum experimental conditions.

## 2. Experiment

2.1. *Preparation Method of Mesoporous Silica Loaded with TiO<sub>2</sub>*. Table 1 lists the physical properties of mesoporous silica loaded with TiO<sub>2</sub>, which has the following characteristics

- (i) Average pore size is in nanoscale. Since the molecular diameter of CO and O<sub>2</sub> is relatively close to the average pore diameter, the high adsorption performance is expected.
- (ii) TiO<sub>2</sub> particle is located inside of pores of the mesoporous silica. Light can pass through mesoporous silica, and gases can also get into the pores of mesoporous silica through the diffusion, therefore, good photocatalytic reaction as well as good adsorption performance can be expected.

Figure 1 shows the preparation method of mesoporous silica particles loaded with TiO<sub>2</sub> in our laboratory, which is developed by referring to the literatures [21–23]. P25 (Degussa, P25, JAPAN AEROSIL Corp., LTD.) powder was selected as TiO<sub>2</sub> source to load. Because of the primary particle size of P25 which is ranged between 20 nm and 30 nm, P25 is suitable for being inserted into the mesoporous silica particle whose size is ranged between 30 nm and 100 nm generally. P25 plays the role of the core for forming mesoporous silica. The pores of mesoporous silica are formed in or around the particles of P25 as illustrated in Figure 2 [23]. Figure 3 shows TEM image of prepared mesoporous silica particles loaded with TiO<sub>2</sub> to understand the structure illustrated in Figure 2. The ratio of loaded TiO<sub>2</sub> to mesoporous silica was controlled by the amount of P25 added to the mixture solution of ion-exchange water, CH<sub>3</sub>(CH<sub>2</sub>)<sub>15</sub>N(CH<sub>3</sub>)<sub>3</sub>Br (purity of 99 wt%, Nacalai Tesque

Corp.),  $(\text{C}_2\text{H}_5\text{O})_4\text{Si}$  (purity of 95 wt%, Nacalai Tesque Corp.), and  $\text{NH}_3$  (purity of 28 wt%, Nacalai Tesque Corp.). The amount of P25 particle added to mixture solution was 0.05 g, 0.54 g, 0.86 g, 1.18 g, 2.10 g, 7.30 g, and 19.5 g for the ratio of 1 wt%, 10 wt%, 15 wt%, 20 wt%, 30 wt%, 60 wt%, and 80 wt%, respectively. Here, the ratio of loaded  $\text{TiO}_2$  is named after preparation condition since it is very difficult to measure the weight of  $\text{TiO}_2$  in mesoporous silica particle directly after preparation process. Particle size of agglomerated mesoporous silica particles loaded with  $\text{TiO}_2$  was sieved into the range between 2.0 mm and 5.6 mm after burning.

**2.2. Experimental Apparatus and Procedure.** Figure 4 illustrates the experimental apparatus which consists of a reactor, a gas mixing chamber, a mass flow controller (MODEL 3660, KOFLOC), a dew point meter (HMT337, VAISALA), a regulator, and a gas cylinder. The reactor, which is a batch type, consists of stainless steel pipe (450 mm (*L.*)  $\times$  60.5 mm (*O.D.*)  $\times$  2.5 mm (*t.*); reaction space 50 mm (*L.*)  $\times$  55.5 mm (*I.D.*)) which includes two acrylic cylinders to cover both ends of UV lamp in it, gas supply and exhaust pipe, valves, gas sampling tap, and UV lamp (FL15BLB, TOSHIBA Co., 436 mm (*L.*)  $\times$  25.5 mm (*D.*)) located at the center of stainless steel pipe. The reaction space for charging gas and filling  $\text{TiO}_2$  particles is  $9.22 \times 10^4 \text{ mm}^3$ . The central wavelength and mean light intensity of UV light is 352 nm and  $4.34 \text{ mW/cm}^2$ , respectively. This light intensity is almost the same as the UV intensity in solar radiation at daytime in the summer of Japan.

In the experiment,  $\text{O}_2$  (purity of 99.9999 vol%) and the premixed gas of  $\text{H}_2$  and CO ( $\text{H}_2$ : 99 vol%, CO: 1 vol%) were mixed in the gas mixing chamber before being supplied to the reactor. By adjusting the flow rate and the pressure of the gases, the initial concentration of  $\text{O}_2$  to CO could be controlled. This remixed gas was charged into the reactor, and the concentration and pressure of gases were confirmed before starting the experiment. The ratios of gasses were charged as  $\text{CO}:\text{O}_2 = 1:0.5, 1:1, 1:2, 1:4, 1:6, 1:8, \text{ and } 1:10$  (balanced by  $\text{H}_2$ ). Although 1 mol CO reacts with 0.5 mol  $\text{O}_2$  theoretically as shown in the reaction of (10), it is necessary to confirm the practical optimum initial concentration ratio of  $\text{O}_2$  to CO in rich  $\text{H}_2$  environment.

The total pressure in the reactor was set at 0.1 MPa. The gas temperature in the reactor was kept at about 300 K during the experiment. Before the mixed gas for CO oxidization was supplied, mesoporous silica particles loaded with  $\text{TiO}_2$  were filled into the reactor by 50 vol% of full reactor volume size.

The experiment was started when illumination of UV light was applied. The gas in reactor was sampled hourly during the experiment. The gas excluding  $\text{H}_2\text{O}$  vapor samples was analyzed by TCD gas chromatograph (VARIAN micro-GC CP-4900, GL Science Corp.) equipped with double columns of Molsieve 5A and PoraPLOT Q. The minimum resolution of the gas chromatograph was 1 ppmV. The concentration of  $\text{H}_2\text{O}$  vapor in the experimental apparatus was measured by the dew point meter whose minimum resolution was 1 ppmV.

### 3. Results and Discussion

**3.1. Effect of Loading Ratio of  $\text{TiO}_2$  on CO Oxidization Performance.** Figures 5 and 6 show the concentration change of  $\text{CO}_2$  and CO with UV light illumination time for the different loading ratios of  $\text{TiO}_2$ . From these figures, it can be seen that the concentration of CO for each loading ratio of  $\text{TiO}_2$  is decreased with the increase of UV light illumination time, while the concentration of  $\text{CO}_2$  is increased. Although the amount of CO reduced does not match the amount of  $\text{CO}_2$  produced which is predicted by (9), the reason of it is that the CO adsorption performance of prepared mesoporous silica loaded with  $\text{TiO}_2$  is different among different loading ratios. The increase ratio of  $\text{CO}_2$  with time is estimated by the following regression line which is derived according to the tendency of data plot:

$$[\text{CO}_2] = R_{\text{inc-CO}_2} t, \quad (11)$$

where  $[\text{CO}_2]$  is the concentration of  $\text{CO}_2$  at each time (ppmV),  $R_{\text{inc-CO}_2}$  stands for the increase ratio of  $\text{CO}_2$  (ppmV/h), and  $t$  is the time for UV light illumination (h). According to Figure 5,  $R_{\text{inc-CO}_2}$  is 159 ppmV/h, 412 ppmV/h, 493 ppmV/h, 706 ppmV/h, 542 ppmV/h, 527 ppmV/h, and 259 ppmV/h for loading ratio of  $\text{TiO}_2$  of 1 wt%, 10 wt%, 15 wt%, 20 wt%, 30 wt%, 60 wt%, and 80 wt%, respectively.  $R_{\text{inc-CO}_2}$  is larger with the increase in loading ratio of  $\text{TiO}_2$  up to 20 wt%, while it becomes smaller with the increase in loading ratio of  $\text{TiO}_2$  from 30 wt%. Although the amount of  $\text{TiO}_2$  loaded in mesoporous silica is increased with the increase in loading ratio of  $\text{TiO}_2$ , which alludes to that the CO oxidization performance is promoted with the increase in the loading ratio of  $\text{TiO}_2$ , the optimum loading ratio of  $\text{TiO}_2$  is in the middle ratio.

To compare the oxidization rate of CO, Figure 7 shows the change of residual ratio of CO with UV light illumination time for different loading ratios of  $\text{TiO}_2$ . The residual ratio of CO is defined as

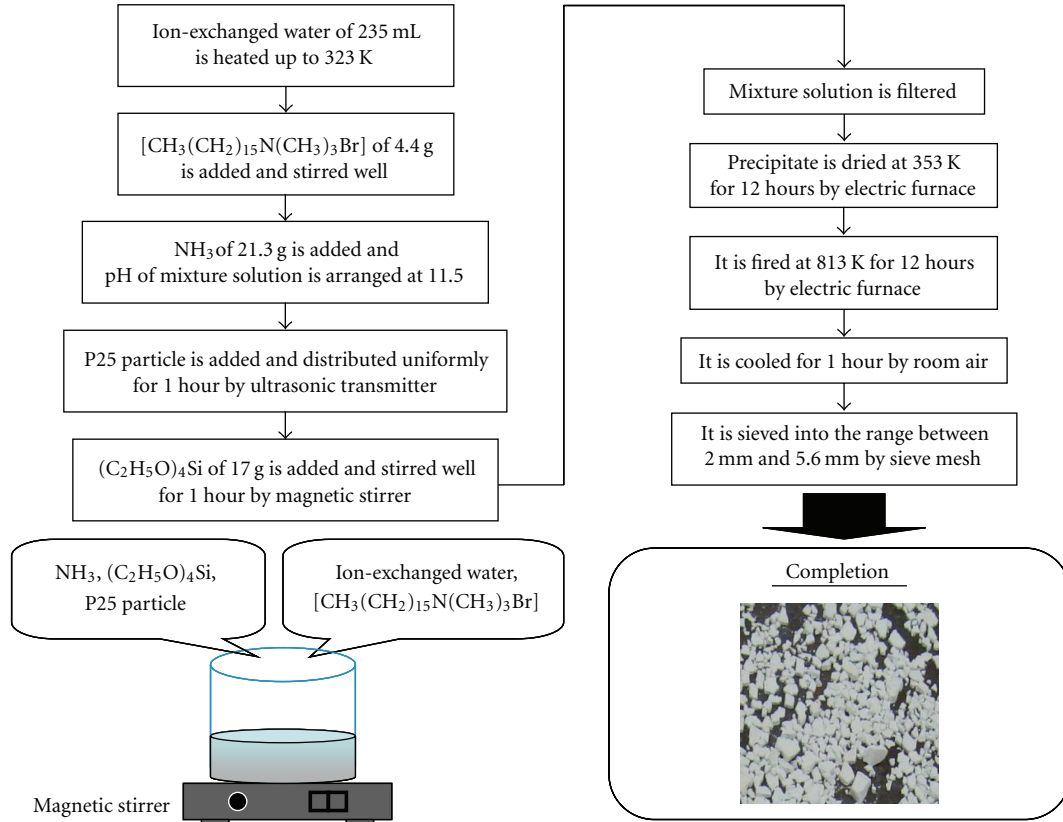
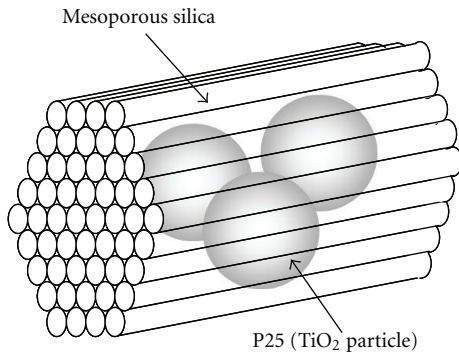
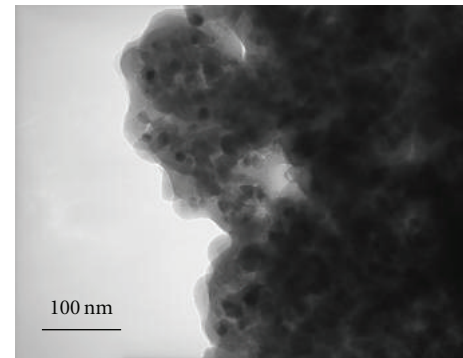
$$R_{\text{res-CO}} = \frac{[\text{CO}]}{[\text{CO}]_0} \times 100, \quad (12)$$

where  $R_{\text{res-CO}}$  stands for the residual ratio of CO (%),  $[\text{CO}]$  is the concentration of CO at each time (ppmV), and  $[\text{CO}]_0$  is the initial concentration of CO at the beginning of the experiment (ppmV). Regression line is derived according to the tendency of data plot:

$$R_{\text{res-CO}} = 100e^{-\alpha t}, \quad (13)$$

where  $\alpha$  is the coefficient of CO removal (1/h). According to Figure 7, the  $\alpha$  which indicates the oxidization rate of CO is  $9.40 \times 10^{-3}$ ,  $8.30 \times 10^{-2}$ ,  $1.31 \times 10^{-1}$ ,  $1.11 \times 10^{-1}$ ,  $1.42 \times 10^{-1}$ ,  $9.81 \times 10^{-2}$ , and  $2.54 \times 10^{-2}$ , for loading ratio of  $\text{TiO}_2$  of 1 wt%, 10 wt%, 15 wt%, 20 wt%, 30 wt%, 60 wt% and 80 wt%, respectively.  $\alpha$  is larger with the increase in loading ratio of  $\text{TiO}_2$  up to 30 wt%, after that, it is smaller with the increase in loading ratio of  $\text{TiO}_2$ .

Figure 8 shows the comparison of selection ratio of CO oxidization among different loading ratios of  $\text{TiO}_2$ .

FIGURE 1: Preparation method of mesoporous silica loaded with TiO<sub>2</sub>.FIGURE 2: Schematic drawing of mesoporous silica loaded with TiO<sub>2</sub>.

Acceleration voltage: 200 kV, × 130.000

FIGURE 3: TEM image of mesoporous silica loaded with TiO<sub>2</sub> particles for the ratio of loaded TiO<sub>2</sub> of 15 wt%.

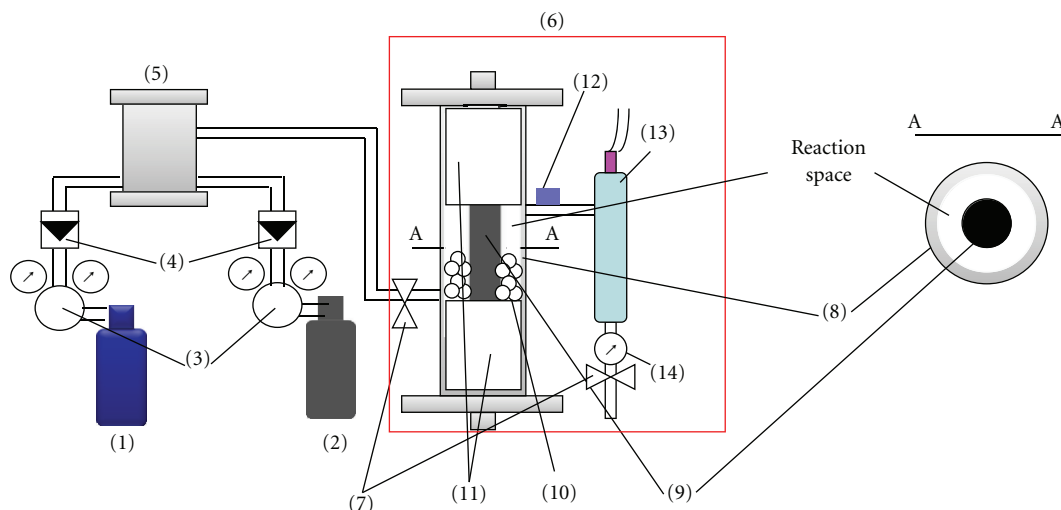
The selection ratio of CO oxidation is calculated by the following equation:

$$R_{\text{sel-CO}} = \frac{[\text{CO}_2] - [\text{CO}_2]_0}{([\text{CO}_2] - [\text{CO}_2]_0) + ([\text{H}_2\text{O}] - [\text{H}_2\text{O}]_0)} \times 100, \quad (14)$$

where  $R_{\text{sel-CO}}$  stands for the selection ratio of CO oxidation (%),  $[\text{CO}_2]$  is the concentration of CO<sub>2</sub> at each time (ppmV),  $[\text{CO}_2]_0$  is the initial concentration of CO<sub>2</sub> at the beginning of the experiment (ppmV),  $[\text{H}_2\text{O}]$  is the concentration of H<sub>2</sub>O vapor at each time (ppmV), and  $[\text{H}_2\text{O}]_0$  is the

initial concentration of H<sub>2</sub>O vapor at the beginning of the experiment (ppmV). In this study, the selection ratio of CO oxidation means the ratio of amount of CO<sub>2</sub> to total oxide.

From this figure, it is known that the middle loading ratios are better compared with the lower and higher loading ratio conditions. Above all, the best selection ratio of CO oxidation is obtained for the loading ratio of TiO<sub>2</sub> of 20 wt%. Considering the results including  $R_{\text{inc-CO}_2}$  and  $\alpha$ , it can be said that mesoporous silica loaded with TiO<sub>2</sub> has



- |   |  |                       |
|---|--|-----------------------|
| (1) Premixed gas cylinder<br>(H <sub>2</sub> : 99 vol%, CO: 1 vol%) | (6) Reactor                                | (11) Acrylic cylinder |
| (2) O <sub>2</sub> gas cylinder<br>(99.9999 vol%)                   | (7) Valve                                  | (12) Sampling tap     |
| (3) Regulator   | (8) Stainless pipe                         | (13) Dew point meter  |
| (4) Mass flow controller  | (9) UV lamp                                | (14) Pressure meter   |
| (5) Gas mixing chamber  | (10) TiO <sub>2</sub> combined with silica |                       |

FIGURE 4: Experimental apparatus.

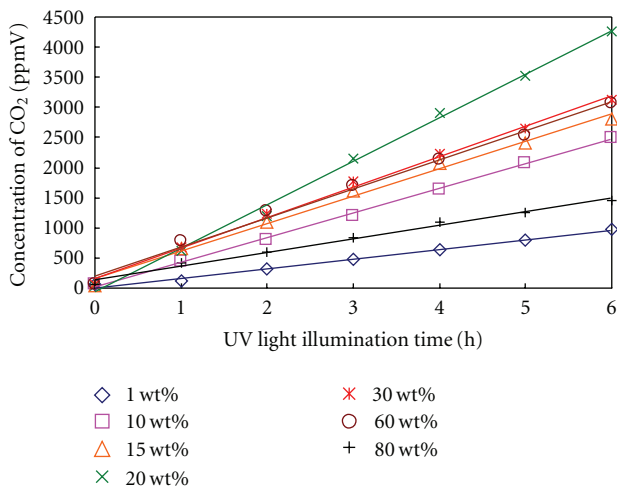


FIGURE 5: Change of concentration of CO<sub>2</sub> with UV light illumination time for different loading ratios of TiO<sub>2</sub>.

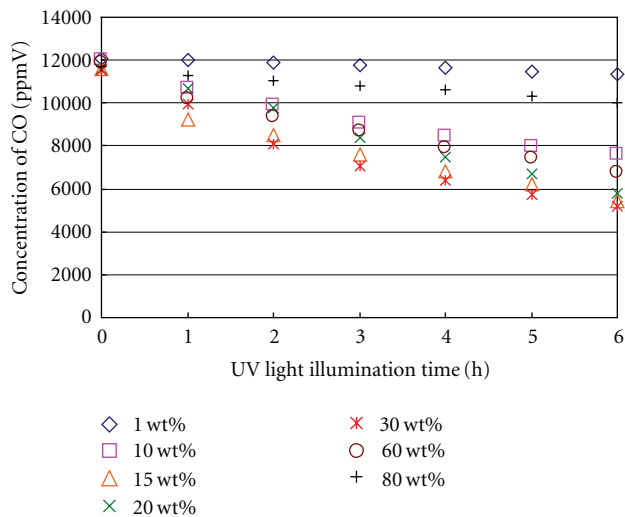


FIGURE 6: Change of concentration of CO with UV light illumination time for different loading ratios of TiO<sub>2</sub>.

the best CO oxidation performance in the middle loading ratio, that is, around 20 wt%. According to our previous study [20], the amount of TiO<sub>2</sub>, that is, the number of TiO<sub>2</sub> particle in mesoporous silica is increased with the increase in loading ratio of TiO<sub>2</sub>. However, the adsorption performance of mesoporous silica loaded with TiO<sub>2</sub> is dropped with the increase in loading ratio of TiO<sub>2</sub> due to the pore diameter expansion and the weakening of the honeycomb shape

of mesoporous silica by increased loaded TiO<sub>2</sub>. Therefore, it can be thought that the best match loading condition between high photocatalytic reaction performance and high adsorption performance is obtained in the middle loading ratio for the mesoporous silica loaded with TiO<sub>2</sub>.

To evaluate the CO oxidation performance of mesoporous silica loaded with TiO<sub>2</sub> from diverse view points, the summation of the performance comparison factor  $F$  which is

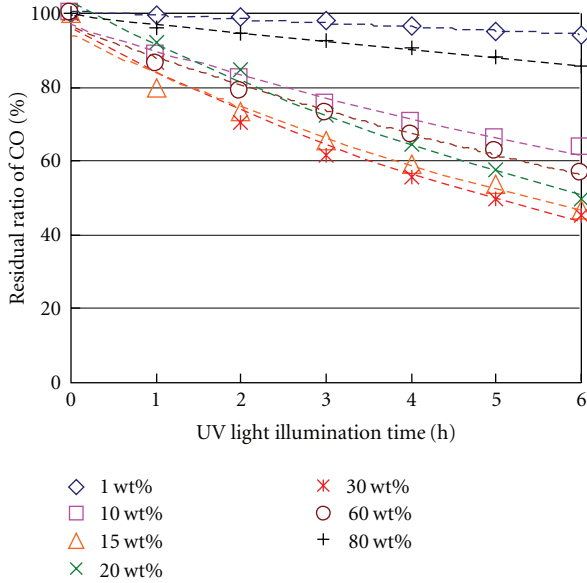


FIGURE 7: Residual ratio of CO for different loading ratio of TiO<sub>2</sub>.

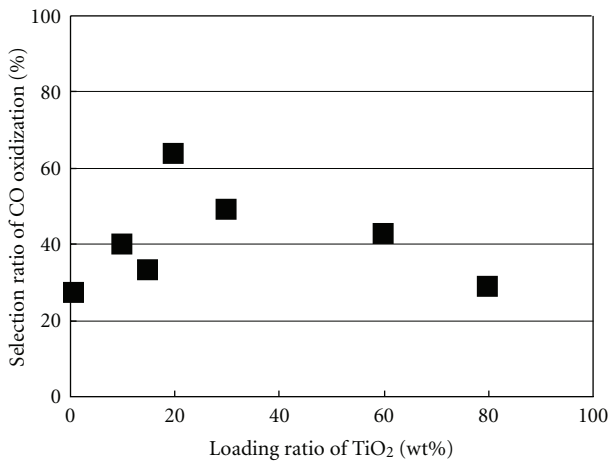


FIGURE 8: Comparison of selection ratio of CO oxidation among different loading ratio of TiO<sub>2</sub>.

calculated by (15) is introduced:

$$F = \frac{\text{Index}_{\text{each}} - \text{Index}_{\text{ave}}}{\text{Index}_{\text{ave}}}, \quad (15)$$

where  $\text{Index}_{\text{each}}$  and  $\text{Index}_{\text{ave}}$  stand for the value of evaluation index on CO oxidation performance such as  $R_{\text{inc-CO}_2}$ ,  $\alpha$ , and  $R_{\text{sel-CO}}$  under each loading ratio of TiO<sub>2</sub>, and the average value of evaluation index on CO oxidation performance among all loading ratios of TiO<sub>2</sub>, respectively. Here, the data after UV light illumination of 6 hours are used to calculate  $F$  for  $\alpha$  and  $R_{\text{sel-CO}}$ .

Table 2 lists  $F$  and the summation of  $F$  for each loading ratio of TiO<sub>2</sub>. From this table, it reveals that the loading ratio of TiO<sub>2</sub> of 20 wt% is the best loading condition. Although the middle loading ratio of TiO<sub>2</sub> was clarified to be suitable for CO oxidation in our previous study [20], the current

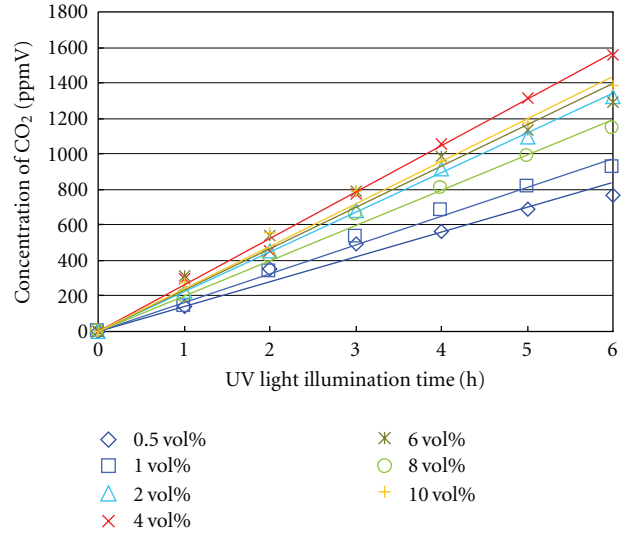


FIGURE 9: Change of concentration of CO<sub>2</sub> with UV light illumination time for different initial concentrations of O<sub>2</sub>.

study confirms that the loading ratio of TiO<sub>2</sub> of 20 wt% is the optimum loading ratio for the promotion of the CO oxidation performance of mesoporous silica loaded with TiO<sub>2</sub>.

**3.2. Effect of Initial Ratio of O<sub>2</sub> to CO on CO Oxidation Performance.** Figures 9 and 10 show the concentration change of CO<sub>2</sub> and CO with UV light illumination time for the different initial concentrations of O<sub>2</sub>. From these figures, it can be seen that the concentration of CO for each initial concentration of O<sub>2</sub> is decreased with the increase in UV light illumination time, while the concentration of CO<sub>2</sub> is increased. According to Figure 9,  $R_{\text{inc-CO}_2}$  is 139 ppmV/h, 162 ppmV/h, 223 ppmV/h, 260 ppmV/h, 232 ppmV/h, 198 ppmV/h, and 239 ppmV/h for initial concentration of O<sub>2</sub> of 0.5 vol%, 1 vol%, 2 vol%, 4 vol%, 6 vol%, 8 vol%, and 10 vol%, respectively. Figure 11 shows the change of residual ratio of CO with UV light illumination time for different initial concentrations of O<sub>2</sub>.  $\alpha$  is  $1.43 \times 10^{-2}$ ,  $2.88 \times 10^{-2}$ ,  $4.62 \times 10^{-2}$ ,  $5.23 \times 10^{-2}$ ,  $4.00 \times 10^{-2}$ ,  $3.97 \times 10^{-2}$ , and  $4.43 \times 10^{-2}$  for initial concentration of O<sub>2</sub> of 0.5 vol%, 1 vol%, 2 vol%, 4 vol%, 6 vol%, 8 vol% and 10 vol%, respectively. From these results, it is confirmed that the initial concentration of O<sub>2</sub> exceeding the stoichiometric ratio, that is, 0.5 vol%, is necessary. In addition,  $R_{\text{inc-CO}_2}$  and  $\alpha$  are increased with the initial concentration of O<sub>2</sub> up to 4 vol% and decreased over 4 vol%. Since the experimental apparatus in this study is a batch type and forcible gas mixing is not carried out, it might be thought that excess amount of O<sub>2</sub> is necessary for O<sub>2</sub> to contact with CO near the surface of mesoporous silica particle loaded with TiO<sub>2</sub>. However, the excess amount of O<sub>2</sub> is thought also to block the diffusions of CO to the surface and CO<sub>2</sub> from the surface. Consequently, there is an optimum initial concentration of O<sub>2</sub> existing.

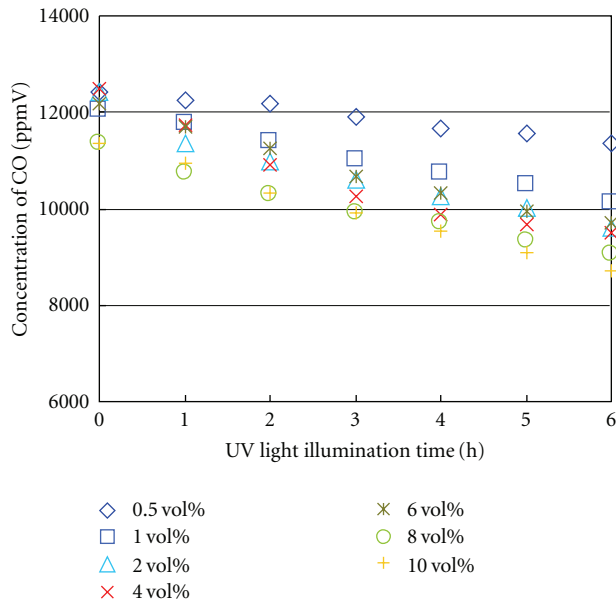
Figure 12 shows the comparison of selection ratio of CO oxidation among different initial concentrations of O<sub>2</sub>.

TABLE 2: Comparison of  $F$  and the summation of  $F$  for each loading ratio of  $\text{TiO}_2$ .

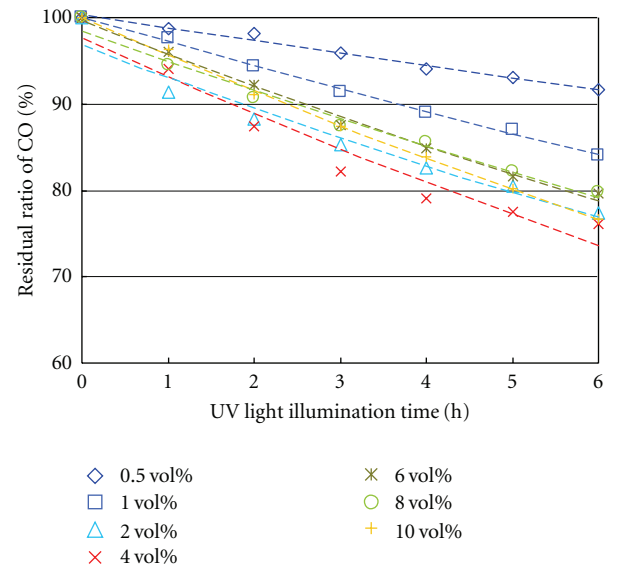
Loading ratio of $\text{TiO}_2$ (wt%)	$R_{\text{inc-CO}_2}$	$F$ (—)		$\sum F$ (—)
		$\alpha$	$R_{\text{sel-CO}}$	
1	-0.60	-0.87	-0.29	-1.76
10	0.027	0.11	0.045	0.18
15	0.23	0.75	-0.13	0.85
20	0.76	0.48	0.67	1.91
30	0.35	0.89	0.29	1.53
60	0.31	0.31	0.11	0.73
80	-0.35	-0.66	-0.25	-1.26

TABLE 3: Comparison of  $F$  and the summation of  $F$  for each initial concentration of  $\text{O}_2$ .

Initial concentration of $\text{O}_2$ (vol%)	$R_{\text{inc-CO}_2}$	$F$ (—)		$\sum F$ (—)
		$\alpha$	$R_{\text{sel-CO}}$	
0.5	-0.33	-0.62	-0.37	-1.32
1	-0.22	-0.24	-0.32	-0.78
2	0.074	0.22	0.23	0.52
4	0.25	0.38	0.35	0.98
6	0.12	0.054	0.29	0.46
8	-0.046	0.046	-0.17	-0.17
10	0.15	0.17	-0.013	0.31

FIGURE 10: Change of concentrations of CO with UV light illumination time for different initial concentrations of  $\text{O}_2$ .

From this figure, it is known that the best selection ratio of CO oxidization is obtained for the initial concentration of  $\text{O}_2$  of 4 vol%, the same as the results of  $R_{\text{inc-CO}_2}$  and  $\alpha$  as described above. With the lower initial concentration of  $\text{O}_2$ , it seems that the CO oxidization performance is not good due to lack of gas supply to the reaction surface as mentioned above. On the other hand, CO oxidization performance declines at the higher initial concentration of  $\text{O}_2$ . Since  $\text{H}_2\text{O}$  that is a byproduct in this reaction is

FIGURE 11: Residual ratio of CO for different initial concentrations of  $\text{O}_2$ .

adsorbed by mesoporous silica more easily than  $\text{CO}$ ,  $\text{O}_2$  and  $\text{CO}_2$  [24], the CO adsorption by mesoporous silica might be dropped under the higher initial concentration of  $\text{O}_2$ . Therefore, the CO oxidization performance of mesoporous silica loaded with  $\text{TiO}_2$  also declines. Consequently, the optimum initial concentration of  $\text{O}_2$  is in the middle level of initial concentration of  $\text{O}_2$ . Table 3 lists  $F$  and the summation of  $F$  for each initial concentration of  $\text{O}_2$ . From this table, it is revealed that the initial concentration of  $\text{O}_2$  of 4 vol%



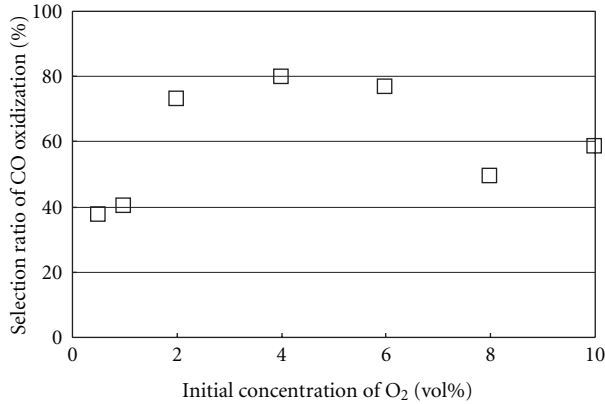


FIGURE 12: Comparison of selection ratio of CO oxidation among different initial concentrations of O<sub>2</sub>.

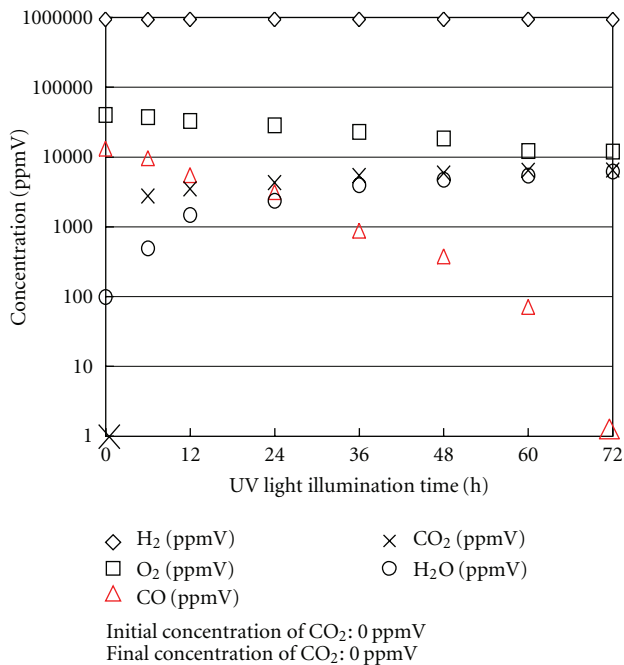


FIGURE 13: Change of each gas concentration with UV light illumination time in the long time experiment (loading ratio of TiO<sub>2</sub> of 20 wt%, initial concentrations of O<sub>2</sub> of 4 vol%).

is also the best initial concentration from diverse view points. Therefore, the optimum initial concentration of O<sub>2</sub> to promote the CO oxidation performance of mesoporous silica loaded with TiO<sub>2</sub> is decided at 4 vol%.

**3.3. Evaluation on the Maximum CO Oxidization Performance of Mesoporous Silica Loaded with TiO<sub>2</sub>.** The above described results are evaluated by UV light illumination of 6 hours. To evaluate the maximum CO oxidation performance of mesoporous silica loaded with TiO<sub>2</sub>, a longer time experiment was carried out under the optimum experimental condition as decided above.

Figure 13 shows the change of each gas concentration with UV light illumination time in the long time experiment with loading ratio of TiO<sub>2</sub> of 20 wt% and initial concentration of O<sub>2</sub> of 4 vol%. From this figure, the concentration of CO could decrease from 12000 ppmV down to 0 ppmV after UV light illumination time of 72 hours. In other words, although taking longer time, the CO was finally eliminated, which is comparable or superior to the results of the other CO oxidation processes [18, 19, 25, 26]. This proves that the proposed technology of TiO<sub>2</sub> combined with silica is a promising alternative CO oxidation process. To promote the CO oxidation performance of mesoporous silica loaded with TiO<sub>2</sub>, that is, to promote the CO oxidation rate further, the investigation on the gas supply and adsorption control and UV light illumination intensity in reactor is thought to be the next subject to study.

## 4. Conclusions

Based on the above experimental results and discussion, the following conclusions can be drawn from this experimental study.

The optimum loading ratio of TiO<sub>2</sub> is around 20 wt% and the optimum initial concentration of O<sub>2</sub> is 4 vol% from the viewpoint of best matching of reaction rate of CO oxidation and selection ratio of CO oxidation. The best match loading condition between high photocatalytic reaction performance and high adsorption performance is in the middle loading ratio for the mesoporous silica loaded with TiO<sub>2</sub>.


The initial concentration of O<sub>2</sub> in excess of the stoichiometric ratio is necessary to ensure enough gas supplied to the reaction surface. However, too much excess initial concentration of O<sub>2</sub> would cause the block of gas diffusion to or from the surface which undermines the CO adsorption performance and would produce too much water that was more easily adsorbed by the mesoporous silica particle loaded with TiO<sub>2</sub>, resulting in the drop of the CO oxidation performance.

The CO of 12000 ppmV in the rich H<sub>2</sub> could be completely oxidized after UV light illumination time of 72 hours, which is comparable with the other CO removal methods.

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