Hindawi Publishing Corporation
International Journal of Photoenergy
Volume 2010, Article ID 294217, 9 pages
doi:10.1155/2010/294217

Research Article

Characteristics of Carbon Monoxide Oxidization in Rich Hydrogen by Mesoporous Silica with TiO_2 Photocatalyst

Akira Nishimura,[1] Yutaka Yamano,[1] Tomokazu Hisada,[1] Masafumi Hirota,[1] and Eric Hu[2]

[1] *Division of Mechanical Engineering, Graduate School of Engineering, Mie University, 1577 Kurimamachiya-cho, Tsu 514-8507, Japan*
[2] *School of Mechanical Engineering, The University of Adelaide, Adelaide, SA 5005, Australia*

Correspondence should be addressed to Akira Nishimura, nisimura@mach.mie-u.ac.jp

Received 17 August 2010; Accepted 9 November 2010

Academic Editor: Jimmy Yu

Hydrogen (H_2) 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_2 that is often produced from methane (CH_4). 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_2. The impact of loading ratio of TiO_2 and initial concentration ratio of O_2 to CO on CO oxidization performance is investigated. As a result, the optimum loading ratio of TiO_2 and initial concentration ratio of O_2 to CO were 20 wt% and 4 vol%, respectively, under the experimental conditions. Under this optimum experimental condition, the CO in rich H_2 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_2 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_2 produced from CH_4, CH_3OH, and gasoline.

CH_4 is normally the feedstock to produce H_2 with Ni or Ru as catalyst at the high temperature range of 873 K–973 K through the following reaction:

$$CH_4 + H_2O \longrightarrow CO + 3H_2. \quad (1)$$

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:

$$CO + H_2O \longrightarrow CO_2 + H_2. \quad (2)$$

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

$$CO + \frac{1}{2}O_2 \longrightarrow CO_2. \quad (3)$$

In the H_2 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_2 photocatalyst combined with adsorbent to oxidize CO is being developed recently due to its potential cost and energy saving.

TiO_2 can oxidize CO under illumination of ultraviolet (UV) ray (available in sunlight) through the following reaction scheme [1, 2].

Photocatalytic reaction:

$$TiO_2 + h\nu\ (< 380\,\text{nm}) \longrightarrow h^+ + e^-. \quad (4)$$

Oxidization of CO:

$$CO + h^+ \longrightarrow CO^+. \quad (5)$$

Reduction of O_2*:*

$$O^2 + e^- \longrightarrow O_2^-, \quad (6)$$

$$O_2^- + h^+ \longrightarrow 2O, \quad (7)$$

$$O + e^- \longrightarrow O^-. \quad (8)$$

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

$$CO^+ + O^- \longrightarrow CO_2. \quad (9)$$

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

$$CO + \frac{1}{2}O_2 \longrightarrow CO_2, \quad (10)$$

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

The oxidization process with TiO_2 has the following merits. (1) There is a lot of TiO_2 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_2 is stable in both acid and alkali environments.

Literature survey shows that TiO_2 photocatalyst combined with adsorbent such as activated carbon, zeolite, and silica (SiO_2) was mainly used in environmental purification technologies such as NO_x removal [4–6], decomposition of acetaldehyde [7], dimethylsulfide [8], 2-propoanol [9], degradation of organophosphate and phosphonoglycine [10], and CO_2 reforming into fuel like CH_4 and CH_3OH [11, 12]. The CO oxidization by photocatalyst combined with FeO_x, AL_2O_3, or CeO_x 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_2 or Cr/SiO_2 [18, 19], there is no report on the CO oxidization characteristics of TiO_2 combined with adsorbent except our previous study [20]. Our previous study investigated the effect of different loading methods of TiO_2 to silica on CO oxidization performance. Comparing two types of TiO_2 particle combined with silica, that is, the silica gel particles coated with TiO_2 film and mesoporous silica particles loaded with TiO_2, the amount of oxidized CO per unit mass of TiO_2 for the mesoporous silica particles loaded with TiO_2 was larger than that for silica gel particles coated with TiO_2 film. Therefore, it revealed that loading was a more effective way to make use of TiO_2 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_2.

Table 1: Physical properties of mesoporous silica loaded with TiO_2.

	Mesoporous silica loaded with TiO_2 particles
Particle size (mm)	0.03–0.25 (primary particle)
	2.0–5.6 (agglomerated particle)
Specific surface area (m^2/g)	219–1038
Average pore diameter (nm)	2.7–3.1
Pore volume (mL/g)	0.63–0.94
Ratio of loaded TiO_2 (wt%)	1, 10, 15, 20, 30, 60, 80

Since UV ray can penetrate the mesoporous silica, the particles of mesoporous silica loaded with TiO_2 can be used in a bed-type reactor. The effect of loading ratio of TiO_2 and initial concentration ratio of O_2 to CO on CO oxidization performance was investigated to decide the optimum experimental conditions. The loading ratio of TiO_2 is changed minutely by 1 wt%, 10 wt%, 15 wt%, 20 wt%, 30 wt%, 60 wt%, and 80 wt%. The initial concentration of O_2 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_2 was evaluated under the optimum experimental conditions.

2. Experiment

2.1. Preparation Method of Mesoporous Silica Loaded with TiO_2. Table 1 lists the physical properties of mesoporous silica loaded with TiO_2, which has the following characteristics

(i) Average pore size is in nanoscale. Since the molecular diameter of CO and O_2 is relatively close to the average pore diameter, the high adsorption performance is expected.

(ii) TiO_2 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_2 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_2 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_2 to understand the structure illustrated in Figure 2. The ratio of loaded TiO_2 to mesoporous silica was controlled by the amount of P25 added to the mixture solution of ion-exchange water, $CH_3(CH_2)_{15}N(CH_3)_3Br$ (purity of 99 wt%, Nacalai Tesque

Corp.), $(C_2H_5O)_4Si$ (purity of 95 wt%, Nacalai Tesque Corp.), and 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 TiO_2 is named after preparation condition since it is very difficult to measure the weight of TiO_2 in mesoporous silica particle directly after preparation process. Particle size of agglomerated mesoporous silica particles loaded with 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.*) × 60.5 mm (*O.D.*) × 2.5 mm (*t.*); reaction space 50 mm (*L.*) × 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.*) × 25.5 mm (*D.*)) located at the center of stainless steel pipe. The reaction space for charging gas and filling TiO_2 particles is 9.22×10^4 mm^3. The central wavelength and mean light intensity of UV light is 352 nm and 4.34 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, O_2 (purity of 99.9999 vol%) and the premixed gas of H_2 and CO (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 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 CO : O_2 = 1 : 0.5, 1 : 1, 1 : 2, 1 : 4, 1 : 6, 1 : 8, and 1 : 10 (balanced by H_2). Although 1 mol CO reacts with 0.5 mol O_2 theoretically as shown in the reaction of (10), it is necessary to confirm the practical optimum initial concentration ratio of O_2 to CO in rich 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 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 H_2O 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 H_2O 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 TiO_2 on CO Oxidization Performance. Figures 5 and 6 show the concentration change of CO_2 and CO with UV light illumination time for the different loading ratios of TiO_2. From these figures, it can be seen that the concentration of CO for each loading ratio of TiO_2 is decreased with the increase of UV light illumination time, while the concentration of CO_2 is increased. Although the amount of CO reduced does not match the amount of CO_2 produced which is predicted by (9), the reason of it is that the CO adsorption performance of prepared mesoporous silica loaded with TiO_2 is different among different loading ratios. The increase ratio of CO_2 with time is estimated by the following regression line which is derived according to the tendency of data plot:

$$[CO_2] = R_{\text{inc-}CO_2} t, \tag{11}$$

where $[CO_2]$ is the concentration of CO_2 at each time (ppmV), $R_{\text{inc-}CO_2}$ stands for the increase ratio of 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 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 TiO_2 up to 20 wt%, while it becomes smaller with the increase in loading ratio of TiO_2 from 30 wt%. Although the amount of TiO_2 loaded in mesoporous silica is increased with the increase in loading ratio of TiO_2, which alludes to that the CO oxidization performance is promoted with the increase in the loading ratio of TiO_2, the optimum loading ratio of 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 TiO_2. The residual ratio of CO is defined as

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

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

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

where α is the coefficient of CO removal (1/h). According to Figure 7, the α which indicates the oxidization rate of CO is 9.40×10^{-3}, 8.30×10^{-2}, 1.31×10^{-1}, 1.11×10^{-1}, 1.42×10^{-1}, 9.81×10^{-2}, and 2.54×10^{-2}, for loading ratio of TiO_2 of 1 wt%, 10 wt%, 15 wt%, 20 wt%, 30 wt%, 60 wt% and 80 wt%, respectively. α is larger with the increase in loading ratio of TiO_2 up to 30 wt%, after that, it is smaller with the increase in loading ratio of TiO_2.

Figure 8 shows the comparison of selection ratio of CO oxidization among different loading ratios of TiO_2.

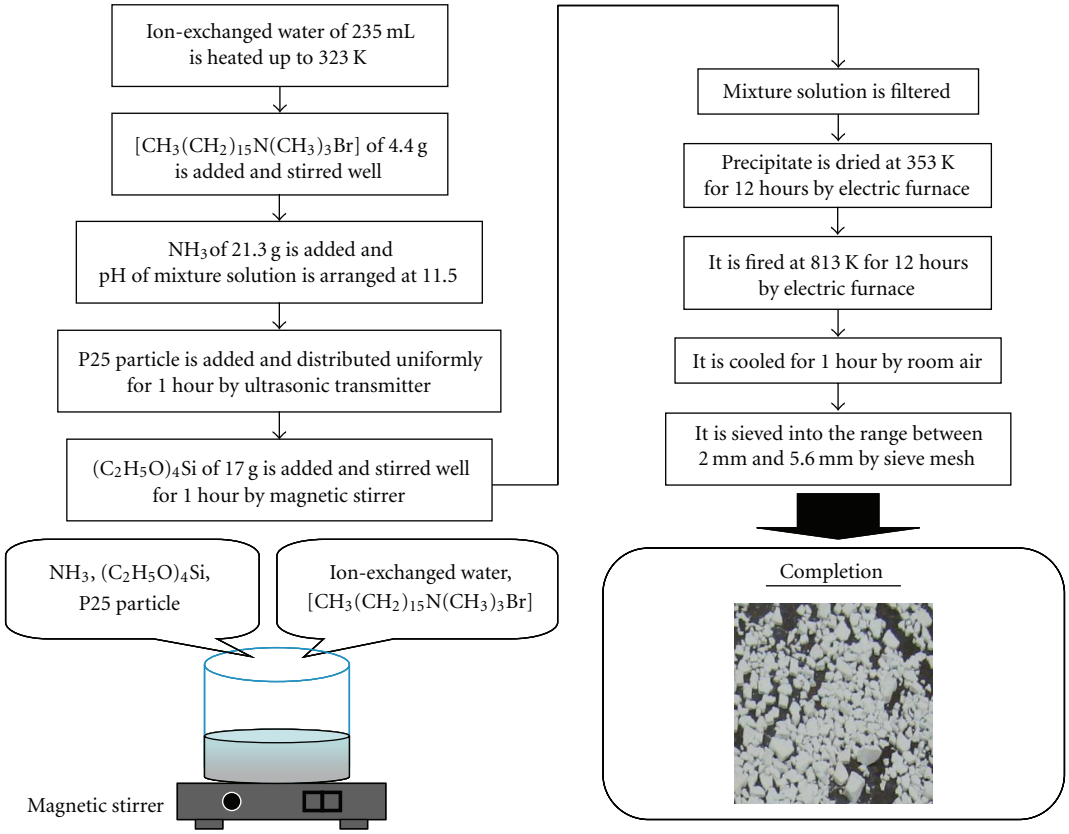


Figure 1: Preparation method of mesoporous silica loaded with TiO_2.

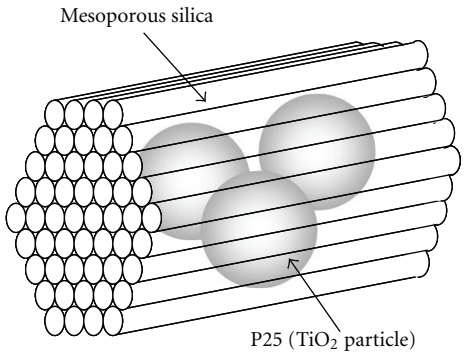
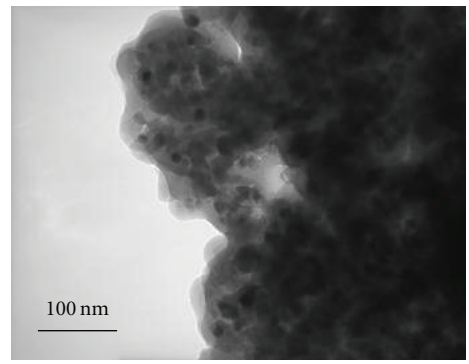


Figure 2: Schematic drawing of mesoporous silica loaded with TiO_2.



Acceleration voltage: 200 kV, × 130.000

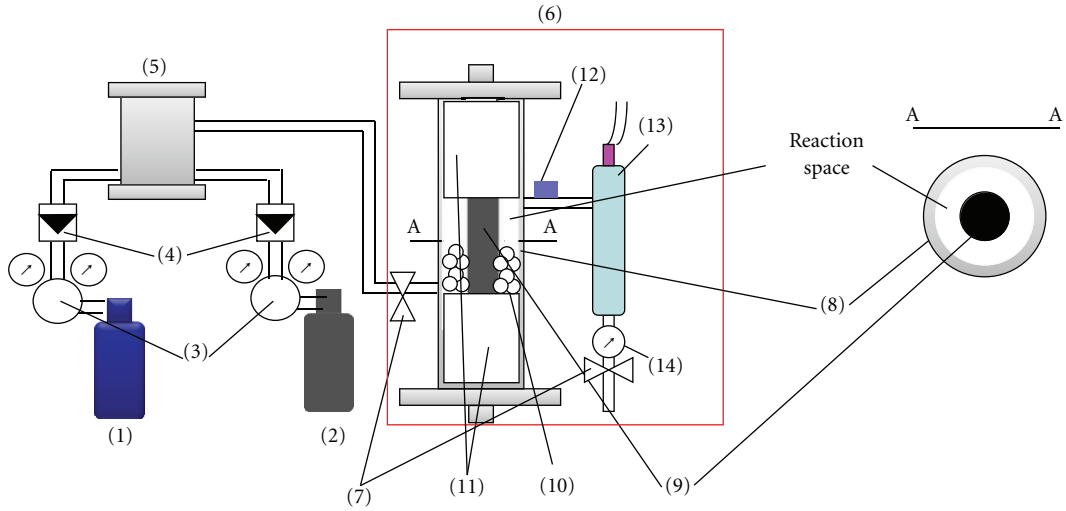
Figure 3: TEM image of mesoporous silica loaded with TiO_2 particlesfor the ratio of loaded TiO_2 of 15 wt%.

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

$$R_{\text{sel-CO}} = \frac{[CO_2] - [CO_2]_0}{([CO_2] - [CO_2]_0) + ([H_2O] - [H_2O]_0)} \times 100, \quad (14)$$

where $R_{\text{sel-CO}}$ stands for the selection ratio of CO oxidization (%), $[CO_2]$ is the concentration of CO_2 at each time (ppmV), $[CO_2]_0$ is the initial concentration of CO_2 at the beginning of the experiment (ppmV), $[H_2O]$ is the concentration of H_2O vapor at each time (ppmV), and $[H_2O]_0$ is the initial concentration of H_2O vapor at the beginning of the experiment (ppmV). In this study, the selection ratio of CO oxidization means the ratio of amount of CO_2 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 oxidization is obtained for the loading ratio of TiO_2 of 20 wt%. Considering the results including $R_{\text{inc-CO}_2}$ and α, it can be said that mesoporous silica loaded with TiO_2 has



(1) Premixed gas cylinder (H_2: 99 vol%, CO: 1 vol%)
(2) O_2 gas cylinder (99.9999 vol%)
(3) Regulator
(4) Mass flow controller
(5) Gas mixing chamber
(6) Reactor
(7) Valve
(8) Stainless pipe
(9) UV lamp
(10) TiO_2 combined with silica
(11) Acrylic cylinder
(12) Sampling tap
(13) Dew point meter
(14) Pressure meter

Figure 4: Experimental apparatus.

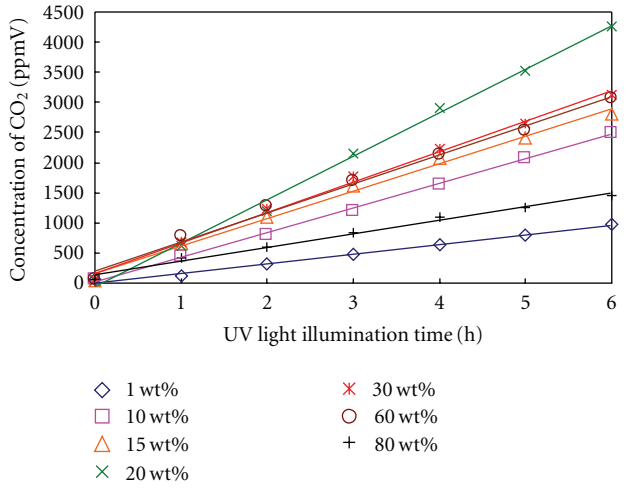


Figure 5: Change of concentration of CO_2 with UV light illumination time for different loading ratios of TiO_2.

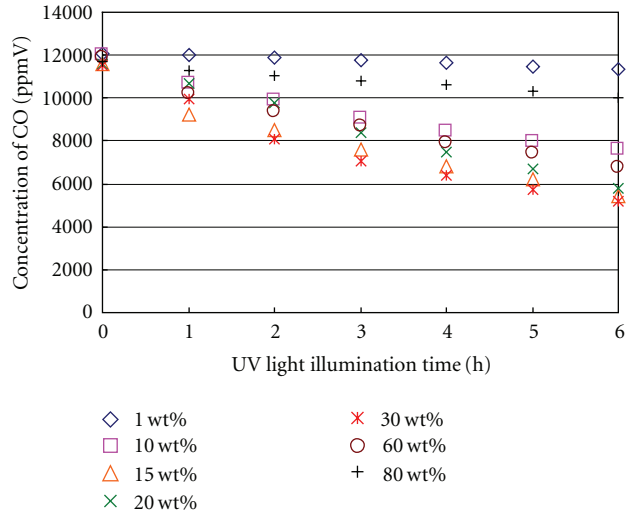


Figure 6: Change of concentration of CO with UV light illumination time for different loading ratios of TiO_2.

the best CO oxidization performance in the middle loading ratio, that is, around 20 wt%. According to our previous study [20], the amount of TiO_2, that is, the number of TiO_2 particle in mesoporous silica is increased with the increase in loading ratio of TiO_2. However, the adsorption performance of mesoporous silica loaded with TiO_2 is dropped with the increase in loading ratio of TiO_2 due to the pore diameter expansion and the weakening of the honeycomb shape of mesoporous silica by increased loaded TiO_2. 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_2.

To evaluate the CO oxidization performance of mesoporous silica loaded with TiO_2 from diverse view points, the summation of the performance comparison factor F which is

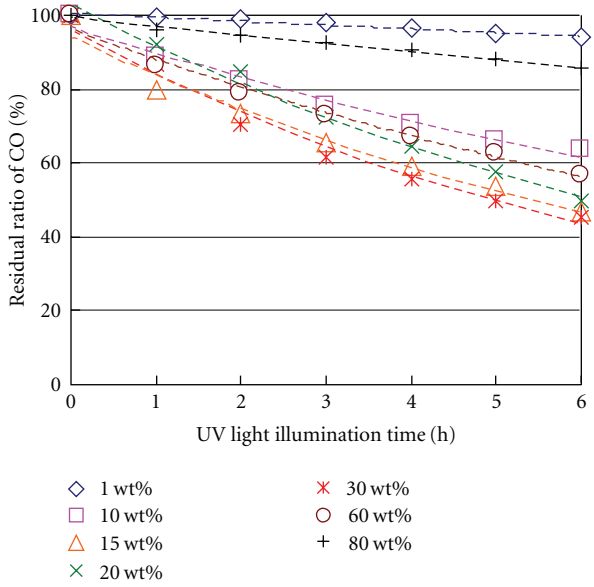


Figure 7: Residual ratio of CO for different loading ratio of TiO_2.

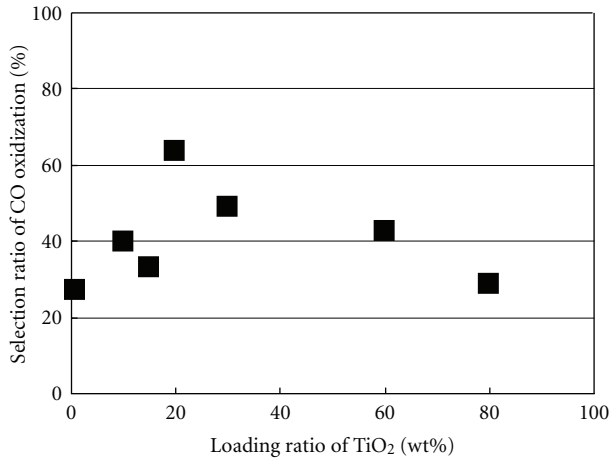


Figure 8: Comparison of selection ratio of CO oxidization among different loading ratio of TiO_2.

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 oxidization performance such as $R_{\text{inc-CO}_2}$, α, and $R_{\text{sel-CO}}$ under each loading ratio of TiO_2, and the average value of evaluation index on CO oxidization performance among all loading ratios of TiO_2, respectively. Here, the data after UV light illumination of 6 hours are used to calculate F for α and $R_{\text{sel-CO}}$.

Table 2 lists F and the summation of F for each loading ratio of TiO_2. From this table, it reveals that the loading ratio of TiO_2 of 20 wt% is the best loading condition. Although the middle loading ratio of TiO_2 was clarified to be suitable for CO oxidization in our previous study [20], the current

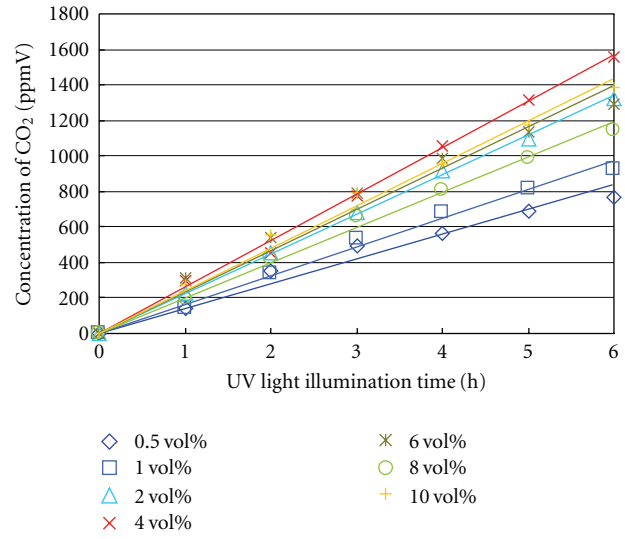


Figure 9: Change of concentration of CO_2 with UV light illumination time for different initial concentrations of O_2.

study confirms that the loading ratio of TiO_2 of 20 wt% is the optimum loading ratio for the promotion of the CO oxidization performance of mesoporous silica loaded with TiO_2.

3.2. Effect of Initial Ratio of O_2 to CO on CO Oxidization Performance. Figures 9 and 10 show the concentration change of CO_2 and CO with UV light illumination time for the different initial concentrations of O_2. From these figures, it can be seen that the concentration of CO for each initial concentration of O_2 is decreased with the increase in UV light illumination time, while the concentration of CO_2 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_2 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_2. α is 1.43×10^{-2}, 2.88×10^{-2}, 4.62×10^{-2}, 5.23×10^{-2}, 4.00×10^{-2}, 3.97×10^{-2}, and 4.43×10^{-2} for initial concentration of O_2 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_2 exceeding the stoichiometric ratio, that is, 0.5 vol%, is necessary. In addition, $R_{\text{inc-CO}_2}$ and α are increased with the initial concentration of O_2 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_2 is necessary for O_2 to contact with CO near the surface of mesoporous silica particle loaded with TiO_2. However, the excess amount of O_2 is thought also to block the diffusions of CO to the surface and CO_2 from the surface. Consequently, there is an optimum initial concentration of O_2 existing.

Figure 12 shows the comparison of selection ratio of CO oxidization among different initial concentrations of O_2.

Table 2: Comparison of F and the summation of F for each loading ratio of TiO_2.

	F (—)			$\sum F$ (—)
Loading ratio of TiO_2 (wt%)	$R_{inc\text{-}CO_2}$	α	$R_{sel\text{-}CO}$	
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 O_2.

	F (−)			$\sum F$(−)
Initial concentration of O_2 (vol%)	$R_{inc\text{-}CO_2}$	α	$R_{sel\text{-}CO}$	
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

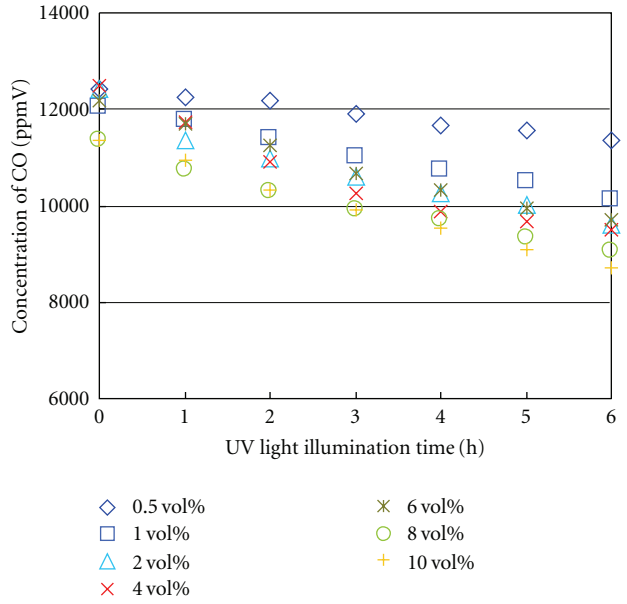


Figure 10: Change of concentrations of CO with UV light illumination time for different initial concentrations of O_2.

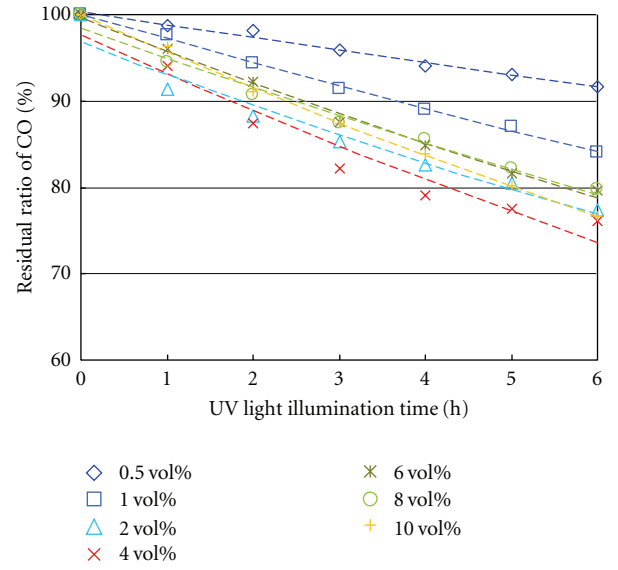


Figure 11: Residual ratio of CO for different initial concentrations of O_2.

From this figure, it is known that the best selection ratio of CO oxidization is obtained for the initial concentration of O_2 of 4 vol%, the same as the results of $R_{inc\text{-}CO_2}$ and α as described above. With the lower initial concentration of 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 O_2. Since H_2O that is a byproduct in this reaction is adsorbed by mesoporous silica more easily than CO, O_2 and CO_2 [24], the CO adsorption by mesoporous silica might be dropped under the higher initial concentration of O_2. Therefore, the CO oxidization performance of mesoporous silica loaded with TiO_2 also declines. Consequently, the optimum initial concentration of O_2 is in the middle level of initial concentration of O_2. Table 3 lists F and the summation of F for each initial concentration of O_2. From this table, it is revealed that the initial concentration of O_2 of 4 vol%

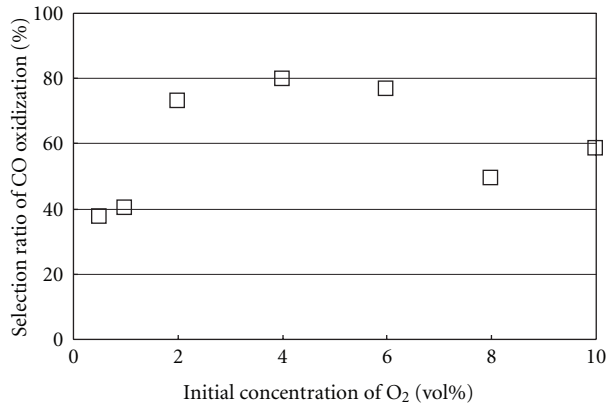


FIGURE 12: Comparison of selection ratio of CO oxidization among different initial concentrations of O_2.

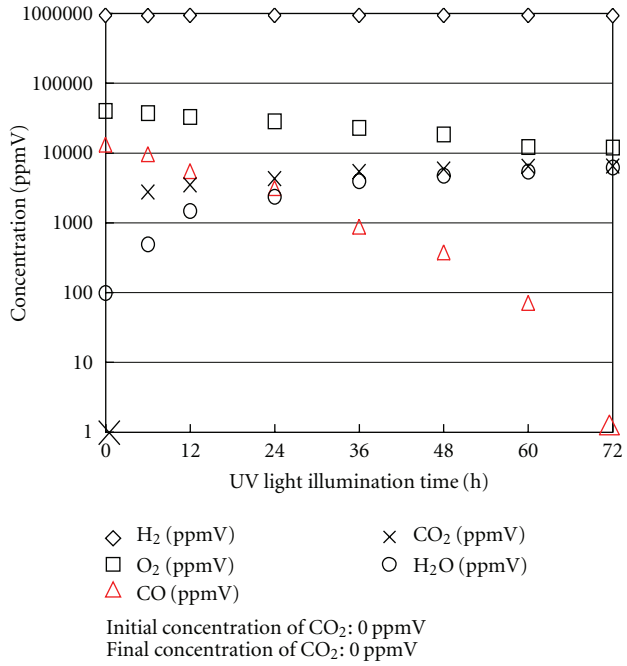


FIGURE 13: Change of each gas concentration with UV light illumination time in the long time experiment (loading ratio of TiO_2 of 20 wt%, initial concentrations of O_2 of 4 vol%).

is also the best initial concentration from diverse view points. Therefore, the optimum initial concentration of O_2 to promote the CO oxidization performance of mesoporous silica loaded with TiO_2 is decided at 4 vol%.

3.3. Evaluation on the Maximum CO Oxidization Performance of Mesoporous Silica Loaded with TiO_2. The above described results are evaluated by UV light illumination of 6 hours. To evaluate the maximum CO oxidization performance of mesoporous silica loaded with TiO_2, 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_2 of 20 wt% and initial concentration of O_2 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 oxidization processes [18, 19, 25, 26]. This proves that the proposed technology of TiO_2 combined with silica is a promising alternative CO oxidization process. To promote the CO oxidization performance of mesoporous silica loaded with TiO_2, that is, to promote the CO oxidization 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_2 is around 20 wt% and the optimum initial concentration of O_2 is 4 vol% from the viewpoint of best matching of reaction rate of CO oxidization and selection ratio of CO oxidization. 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_2.

The initial concentration of O_2 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_2 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_2, resulting in the drop of the CO oxidization performance.

The CO of 12000 ppmV in the rich H_2 could be completely oxidized after UV light illumination time of 72 hours, which is comparable with the other CO removal methods.

References

[1] Formenti M. and S. J. Teichner, *Catalysis*, Specialist Periodical Report, The Chemical Society, London, UK, 1978.

[2] S. Sato, T. Kadowaki, and K. Yamaguchi, "Photo-isotope exchange between lattice oxygen and gaseous phase oxygen of oxide semiconductor—relationship with photocatalytic activity," *Catalyst*, vol. 27, no. 6, pp. 446–448, 1985.

[3] U.S. Department of the Interior and U.S. Geological Survey, *Mineral Commodity Summaries 2006*, United States Government Printing Office, Washington, DC, USA, 2006.

[4] J. Zhang, M. Minagawa, M. Matsuoka, H. Yamashita, and M. Anpo, "Photocatalytic decomposition of NO on Ti-HMS mesoporous zeolite catalysts," *Catalysis Letters*, vol. 66, no. 4, pp. 241–243, 2000.

[5] H. Kominami, K. Yukishita, T. Kimura et al., "Direct solvothermal formation of nanocrystalline TiO_2 on porous SiO_2 adsorbent and photocatalytic removal of nitrogen oxides in air over TiO_2-SiO_2 composites," *Topics in Catalysis*, vol. 47, no. 3-4, pp. 155–161, 2008.

[6] T. H. Lim and S. D. Kim, "Photocatalytic reduction of NO by CO over TiO_2/Silica gel in an annulus fluidized bed photoreactor," *Journal of the Chinese Institute of Chemical Engineers*, vol. 36, no. 1, pp. 85–89, 2005.

[7] Y. G. Shul, H. J. Kim, S. J. Haam, and H. S. Han, "Photocatalytic characteristics of TiO_2 supported on SiO_2," *Research on Chemical Intermediates*, vol. 29, no. 7–9, pp. 849–859, 2003.

[8] C. Cantau, T. Pigot, R. Brown et al., "Photooxidation of dimethylsulfide in the gas phase: a comparison between TiO_2-silica and photosensitizer-silica based materials," *Applied Catalysis B*, vol. 65, no. 1-2, pp. 77–85, 2006.

[9] K. Yamaguchi, K. Inumaru, Y. Oumi, T. Sano, and S. Yamanaka, "Photocatalytic decomposition of 2-propanol in air by mechanical mixtures of TiO_2 crystalline particles and silicalite adsorbent: the complete conversion of organic molecules strongly adsorbed within zeolitic channels," *Microporous and Mesoporous Materials*, vol. 117, no. 1-2, pp. 350–355, 2009.

[10] G. R. M. Echavia, F. Matzusawa, and N. Negishi, "Photocatalytic degradation of organophosphate and phosphonoglycine pesticides using TiO_2 immobilized on silica gel," *Chemosphere*, vol. 76, no. 5, pp. 595–600, 2009.

[11] K. Ikeue, H. Yamashita, and M. Anpo, "Photocatalytic reduction of CO_2 with H_2O on titanium oxides prepared within zeolites and mesoporous molecular sieves," *Electrochemistry*, vol. 70, no. 6, pp. 402–408, 2002.

[12] H. Yamashita, "Photocatalytic action of highly dispersion TiO_2 prepared within pore of zeolite," in *Proceedings of the 80th Catalytic Society of Japan Meeting Abstracts (CATSJ '97)*, vol. 39, pp. 414–415, 1997.

[13] K. I. Tanaka, Y. Moro-Oka, K. Ishigure et al., "A new catalyst for selective oxidation of CO in H_2 : part 1, activation by depositing a large amount of FeO on Pt/Al_2O_3 and Pt/CeO_2 catalysts," *Catalysis Letters*, vol. 92, no. 3-4, pp. 115–121, 2004.

[14] M. Shou, K. I. Tanaka, K. Yoshioka, Y. Moro-Oka, and S. Nagano, "New catalyst for selective oxidation of CO in excess H_2 designing of the active catalyst having different optimum temperature," *Catalysis Today*, vol. 90, no. 3-4, pp. 255–261, 2004.

[15] K. Tanaka and M. Shou, "Promotion effect of H_2 and H_2O on CO oxidization Reaction," in *Proceedings of the 96th Catalytic Society of Japan Meeting Abstracts (CATSJ '05)*, vol. 47, pp. 418–420, 2005.

[16] M. Watanabe, H. Uchida, H. Igarashi, and M. Suzuki, "Pt catalyst supported on zeolite for selective oxidation of CO in reformed gases," *Chemistry Letters*, pp. 21–22, 1995.

[17] H. Igarashi, H. Uchida, M. Suzuki, Y. Sasaki, and M. Watanabe, "Removal of carbon monoxide from hydrogen-rich fuels by selective oxidation over platinum catalyst supported on zeolite," *Applied Catalysis A*, vol. 159, no. 1-2, pp. 159–169, 1997.

[18] T. Kamegawa, R. Takeuchi, M. Matsuoka, and M. Anpo, "Photocatalytic oxidation of CO with various oxidants by Mo oxide species highly dispersed on SiO_2 at 293 K," *Catalysis Today*, vol. 111, no. 3-4, pp. 248–253, 2006.

[19] T. Kamegawa, M. Matsuoka, and M. Anpo, "Photocatalytic selective oxidation of CO with O_2 in the presence of H_2 over highly dispersed chromium oxide on silica under visible or solar light irradiation," *Research on Chemical Intermediates*, vol. 34, no. 4, pp. 427–434, 2008.

[20] A. Nishimura, T. Hisada, M. Hirota, M. Kubota, and E. Hu, "Using TiO_2 photocatalyst with adsorbent to oxidize carbon monoxide in rich hydrogen," *Catalysis Today*, vol. 158, no. 3-4, pp. 296–304, 2010.

[21] K. Inumaru, M. Murashima, T. Kasahara, and S. Yamanaka, "Enhanced photocatalytic decomposition of 4-nonylphenol by surface-organografted TiO_2: a combination of molecular selective adsorption and photocatalysis," *Applied Catalysis B*, vol. 52, no. 4, pp. 275–280, 2004.

[22] T. Kasahara, K. Inumaru, and S. Yamanaka, "Enhanced photocatalytic decomposition of nonylphenol polyethoxylate by alkyl-grafted TiO_2-MCM-41 organic-inorganic nanostructure," *Microporous and Mesoporous Materials*, vol. 76, no. 1–3, pp. 123–130, 2004.

[23] K. Inumaru, T. Kasahara, M. Yasui, and S. Yamanaka, "Direct nanocomposite of crystalline TiO_2 particles and mesoporous silica as a molecular selective and highly active photocatalyst," *Chemical Communications*, no. 16, pp. 2131–2133, 2005.

[24] S. Y. Jeong, H. Jin, J. M. Lee, and D. J. Yim, "Adsorption on Ti-and Al-containing mesoporous materials prepared from fluorosilicon," *Microporous and Mesoporous Materials*, vol. 44-45, pp. 717–723, 2001.

[25] W. Zhang, Y. Huang, J. Wang et al., "$IrFeO/SiO_2$-a highly active catalyst for preferential CO oxidation in H_2," *International Journal of Hydrogen Energy*, vol. 35, no. 7, pp. 3065–3071, 2010.

[26] N. Maeda, T. Matsushima, M. Kotobuki et al., "HO_2-tolerant monolithic catalysts for preferential oxidation of carbon monoxide in the presence of hydrogen," *Applied Catalysis A*, vol. 370, no. 1-2, pp. 50–53, 2009.