J Mater Sci (2008) 43:4230–4235
DOI 10.1007/s10853-008-2612-3

Catalytic wet oxidations of aromatic compounds over supported copper oxides

Ayumu Onda · Yotaro Suzuki · Shinji Takemasa · Koji Kajiyoshi · Kazumichi Yanagisawa

Received: 26 October 2006 / Accepted: 25 March 2008 / Published online: 9 April 2008

Abstract Catalytic wet oxidations of naphthalene as a model compound of persistent aromatic compounds were carried out with hydrogen peroxide in a closed autoclave lined with Teflon. CuO/Al_2O_3 and CuO/AC catalyst showed the high activity for the naphthalene oxidation with hydrogen peroxide of 1.0 mol L^{-1} at 100 °C. Naphthalene, whose initial concentration was 1.0 g L^{-1}, was converted completely and the concentration of water-soluble organic compounds in the resultant aqueous solution was less than 25 ppm-C. In contrast, platinum, and manganese oxide, silver oxide, and ruthenium oxide catalysts consumed hydrogen peroxide preferentially. Iron and nickel oxides catalysts showed lower activity than the copper oxide catalyst. During the reaction, the intermediate organic acids were formed and then were oxidized. Simultaneously, copper species of CuO catalysts were dissolved and then were precipitated. The precipitated copper species on the catalyst support showed the catalytic activity. CuO/Al_2O_3 catalysts showed high activity for the six successive batch reactions with the treatment of sodium carbonate after the reaction to precipitate copper ions.

Introduction

Wet oxidation with oxygen or hydrogen peroxide as a oxidizing agent has attracted great attention because of its potential applications to decompose and dechlorinate persistent chlorinated organic compounds [1–3], and to purify wastewater containing organic pollutant [4–10].

Phenol is a represented model compound of persistent organic pollutants for wet oxidation studies. Many studies for the catalytic wet oxidation of phenol were reported [4–8, 11–15]. Among many heterogenous catalysts, catalysts based on copper oxides show high activities in the oxidation and are commonly used to study the catalytic wet oxidation of wastewater containing persistent organic pollutant [11]. The copper oxide catalysts show deactivation during the oxidation due to the leaching of copper caused by the exposure of the catalyst to acid aqueous solution [15]. It is difficult to avoid the acid conditions since the final intermediates formed through the oxidation of organic pollutants are short chain acid such as oxalic, formic, and acetic acid.

Naphthalene and its polymers are used as a stabilizing and protecting material of hazardous substances. Disposal of these materials is a problem because naphthalene is a persistent organic compound. Catalytic and non-catalytic oxidations of naphthalene were investigated for the steam reforming of tar in gas phase [16, 17] and for the eliminations of polycyclic aromatic hydrocarbons (PAHs) with oxygen gas in gas phase [18–20] and in supercritical water [21] and with ozone gas at ordinary temperature [22, 23]. In those studies, naphthalene was used as a model compound of tar derived from biomass gasification and PAHs which are environmental pollutants in the exhausts of the diesel vehicles with particulates. The total oxidation of naphthalene with oxygen gas was effectively controlled by heterogeneous catalysts such as platinum supported on alumina [19].

Although naphthalene is known as a water-insoluble compound, the solubility exponentially increases with increasing temperature, such as 28 ppm at 293 K, 61 ppm

A. Onda (✉) · Y. Suzuki · S. Takemasa · K. Kajiyoshi · K. Yanagisawa
Research Laboratory of Hydrothermal Laboratory,
Kochi University, Kochi 780-8520, Japan
e-mail: onda@cc.kochi-u.ac.jp

at 313 K, 128 ppm at 333 K, and 258 ppm at 348 K [24]. Extrapolating those data toward high temperature, it is assumed to be more than 500 ppm at 373 K and more than 1,000 ppm at 393 K. This suggests that hydrothermal treatments might be an attractive method for naphthalene conversion. Hot water is expected as solvent for the oxidations of naphthalene, for example, it was expected for applications in the purification of the polluted water or seawater by crude oil.

In our previous study [25], naphthalene was converted in the wet oxidation without catalysts. In a wet oxidation, the reactants and oxidizing agents contact with not only additional catalysts but also the liner materials of reactors. The liner materials of metals and alloys such as SUS-316 and Hastelloy-C showed the catalytic performance [25]. Teflon is a relatively inert material for many chemicals and shows a relatively high resistance for temperature up to about 500 K. However, Teflon is seriously damaged over about 550 K, and it has low pressure residence and low mechanical strength. In this study, Teflon is used as a liner material and assumed as an inert material with non-catalytic performance for the wet oxidations.

Herein, we report the wet oxidation of naphthalene over metal oxide supported catalysts mainly containing copper oxide with hydrogen peroxide as an oxidizing agent. The resultant solutions are analyzed by gas chromatography, high performance liquid chromatograph, total organic carbon analyzer, the iodometry method, and atomic absorbance spectroscopy. The conversion and mineralization of naphthalene and the successive batch reaction are discussed. To demonstrate the effectiveness and impact of the catalytic wet oxidation of naphthalene, the amount of initially introduced naphthalene corresponded to 1,000 ppm of naphthalene concentration in water which was much higher than the dissolvable amounts at room temperature. In addition, because copper ion is toxic and is a cause of the deactivation of catalysts, the elution and precipitation of copper species during the reaction and the catalytic activity of the precipitated copper species are also considered.

Experimental

Materials

γ-Al_2O_3 (JRC-ALO-2, reference catalyst of the Catalysis Society of Japan) with a surface area of 175 $m^2\ g^{-1}$ was used as the catalyst support in this study. Catalysts were prepared by incipient wetness method with appropriate metal salt solutions: copper (α) nitrate trihydrate (Wako Pure Chemicals Industrials), nickel nitrate hexahydrate (Wako), iron (β) nitrate enneahydrate (Wako), manganese (α) nitrate hexahydrate (Wako), silver nitrate, platinum chloride (Soekawa Chemicals), palladium nitrate *n*-hydrate (Soekawa). SiO_2 (CARiACT Q-6, Fuji Silysia Chemical), TiO_2 (P25, Degussa), MnO_2 (Wako), CeO_2 (Soekawa), and active carbon (Wako) were also used as the catalyst supports for copper oxide catalysts. The metal loadings were 5 wt%. An appropriate amount of solid metal salts was dissolved in 4 mL of distilled deionized water before mixing with 5 g of γ-Al_2O_3. The mixtures were dried in an oven at 60 °C and were then heated by 5 °C min^{-1} and calcined at 450 °C for 4 h. The prepared catalysts were characterized by using BET surface area (Yuasa Ionics, Nova1000), inductively coupled plasma (ICP; Seiko SPS7000A), and X-ray diffraction (XRD; Rigaku Rotaflex RAD-RC).

Experimental setup and procedure

The wet oxidation reactions were carried out in a closed autoclave with inner volume of 20 mL. The sturdy outer part of the autoclave was made of iron. Teflon was used as a liner of autoclave. The high-pressure valve and the autoclave chamber were connected by a Teflon tube for gas sampling (Fig. 1).

Naphthalene (10 mg) and distilled water or hydrogen peroxide aqueous solution (10 mL) were introduced into the autoclaves under air. The filled ratio was 50%. In the case of wet oxidations using oxygen gas, the autoclave including naphthalene and deionized distilled water was filled with 2 MPa of oxygen gas. The autoclave was heated to the desired temperature (323–573 K) by an induction heater with a motor for stirring in rocking motion [3]. The heating rate was 20 K min^{-1}. The temperature was kept for 30 min, and cooled up to room temperature by an electric fan within 15 min. The gas sampler tube was out of the heater and was not heated.

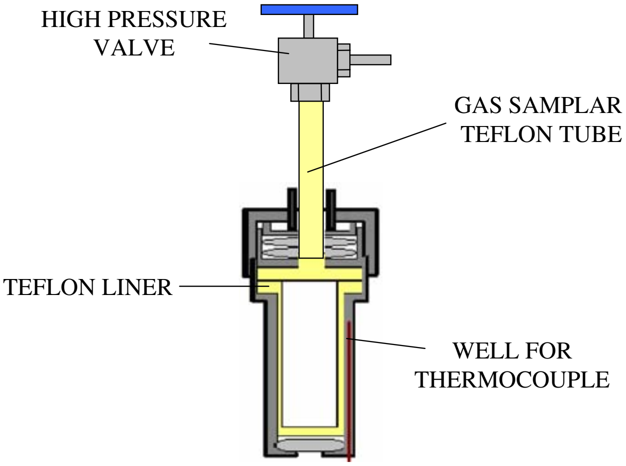

Fig. 1 Autoclave with a Teflon liner

After reaction, the evolved gas was collected to determine the total volume, and the gas was analyzed by GC-TCD (Shimadzu, GC-8A) with an active carbon column (3 mm i.d., 3 m) and by GC-MS (Hewlett-Packard, 6890 Series) with a HP-ProtQ capillary column (0.25 mm i.d., 30 m).

After the filtration, the liquid phase was analyzed by a pH meter (Horiba, F-22), a total organic carbon analyzer (Shimadzu, TOC-5000A), and a high performance liquid chromatograph (Hitachi, L-2130) with double columns of Shodex RSpak KC-811 (8 mm i.d., 300 mm) and a Shodex RSpak KC-G column (6 mm i.d., 50 mm) using a variable wavelength UV monitor. A concentration of remained hydrogen peroxide in the solution was determined by the iodometry method with a sulfuric acid (2 N) aqueous solution with an excess of potassium iodide and the titration with 0.1 M sodium thiosulfate aqueous solution and small amounts of starch as an indicator.

After extractions of remaining naphthalene with ethyl ether conversions of naphthalene were quantified by GC-FID (Shimadzu 14B) with a DB-1 capillary column. The ethyl ether phases were also analyzed by GC-MS (Hewlett-Packard, 6890 Series) with an HP-5MS capillary column (0.25 mm i.d., 30 m). In the case of high conversion of naphthalene, naphthalene in water phase was also determined by the GC-FID. The concentrations of copper ions were determined by atomic adsorption spectroscopy.

Results and discussion

The wet oxidations of naphthalene with hydrogen peroxide over various kinds of supported catalysts

The metal loadings on catalyst supports were determined to be 5 wt% by the ICP analysis. Metals and metal oxides on catalyst supports showed no peak in these XRD patterns except for Pt/Al_2O_3, which might indicate high dispersion of metal species on supports. The catalytic wet oxidation of naphthalene with 1.0 mol L^{-1} of hydrogen peroxide at 100 °C, which was five times more than stoichiometric amounts for total oxidation of naphthalene, are shown in Table 1. In the blank reaction without catalysts, the conversions of naphthalene and hydrogen peroxide and the concentration of intermediate water-soluble organic compounds (WSOCs) were 11.5%, 2%, and 17.7 C-%, respectively. Catalytic properties of the supported catalysts were classified into three groups. The first group included platinum, ruthenium oxide, manganese oxide, and silver oxide catalysts, which consumed preferentially hydrogen peroxide. The conversions of naphthalene were less than 26%. The second group included nickel oxide and alumina catalysts which showed weak catalytic effects for hydrogen peroxide activation. The third group included copper oxide and iron oxide catalysts. Both catalysts showed the highest activity for the conversion of naphthalene. Over CuO/Al_2O_3, the concentration of WSOCs in the resultant aqueous solution was 25 ppm-C which was 2.7 C-% of initially introduced carbon. Carbon dioxide and oxygen were observed as gas products. The CuO/Al_2O_3 catalyst showed the highest activity for the wet oxidation of naphthalene with hydrogen peroxide. In contrast, when 20 bar of oxygen gas was used as an oxidizing agent in the wet oxidation of naphthalene on CuO/Al_2O_3, the reaction temperature was required to be over 180 °C (not shown our data). In literatures [18, 19], the gas-phase oxidations of naphthalene on highly active Pt/Al_2O_3 catalyst were accelerated at 170–210 °C in a fixed bed flow reactor. The oxidation conditions, i.e. pressure and temperature, were lowered by using hydrogen peroxide.

Table 1 The catalytic wet oxidation of naphthalene over metal or metal oxide supported on γ-Al_2O_3.at 100 °C

Catalyst	Conversion/%		Yield/C-%
	Naphthalene	H_2O_2	WSOCs
Blank	11.5	2.0	17.7
Pt	25.7	100	11.7
Ru_O	18.0	100	5.8
Mn_O	9.6	100	6.3
Ag_O[a]	7.3	99.3	6.7
γ-Al_2O_3[b]	20.0	12.0	19.0
Ni_O	9.7	18.5	6.3
Fe_O	100	42.0	28.9
Cu_O	100	100	2.7

Catalyst, 20 mg; Naphthalene, 10 mg; 1.0 mol L^{-1} H_2O_2, 10 mL; Reaction time, 30 min

[a] Silver species might be metallic

[b] No metal species

Effects of the reaction temperature on the wet oxidation with hydrogen peroxide over CuO/Al_2O_3 catalyst

Figure 2 shows the effect of the reaction temperature on the oxidation with and without CuO/Al_2O_3 catalyst. In the blank reaction without catalyst, the naphthalene conversion is less than 30% even at 120 °C. In the reaction over CuO/Al_2O_3 catalyst, naphthalene is significantly converted at 50 °C and completely converted at 80 °C. The reaction temperature over 50 °C might be required for the solubility of naphthalene in water and the activation of hydrogen peroxide [24]. In general, the organic compounds containing oxygen of main WSOCs are formed as intermediates in the wet oxidation of hydrocarbons with oxygen gas or peroxides. As the intermediates, many kinds

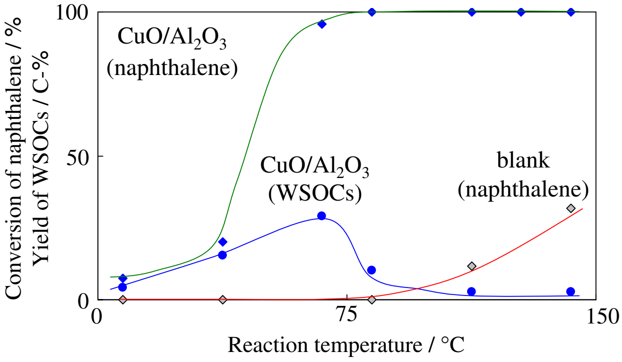

Fig. 2 Effects of the reaction temperature on the oxidation of naphthalene. Naphthalene, 10 mg; $[H_2O_2] = 1.0$ mol L^{-1}; Cu/Al_2O_3, 20 mg or 0 mg; reaction time, 30 min

of organic compounds can be formed such as organic acids, phenolic compounds, and organic peroxides. And then, the WSOCs are finally oxidized into carbon dioxide and water. In Fig. 2, the yield of WSOCs was highest at reaction temperature of 70 °C, and it decreased to 2.7 C-% (25 ppm-C) at 100 °C.

Leaching of Cu species

Figure 3 shows the dependence of reaction time on the yield of WSOCs, the pH value, and the elution of Cu species in the aqueous media. At 5 min of reaction time, yields of WSOCs was 10 C-%, the pH was 4.6. The yields of WSOCs decreased with reaction time, simultaneously the pH increased to neutral. The results indicated that much of WSOCs were organic acids. Acetic and formic acids were observed in the solution by HPLC analysis. In contrast, the amounts of copper ions in the solution decreased with reaction time, which suggested that the Cu species on catalyst support were dissolved and then precipitated during the reaction.

Although a 1.0 mol L^{-1} hydrogen peroxide aqueous solution shows acidic pH of 5, copper ions were not detected in the aqueous media after the reaction at 100 °C on CuO/Al_2O_3 in a 1.0 mol L^{-1} hydrogen peroxide solution without naphthalene. In contrast, copper ions were detected in the aqueous media after the reaction of acetic acid (0.01 mol L^{-1}) at 100 °C on CuO/Al_2O_3 without hydrogen peroxide. The results indicated that copper species were dissolved into the aqueous media by organic acids.

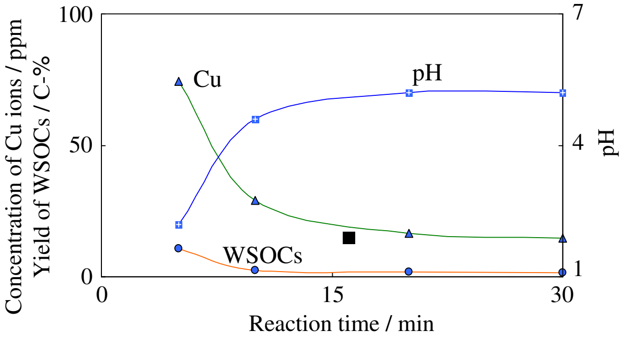

Fig. 3 Leaching of Cu species. Naphthalene, 10 mg; 1.0 M H_2O_2 aqueous solution, 10 mL; CuO/Al_2O_3, 20 mg; Reaction Temperature, 100 °C

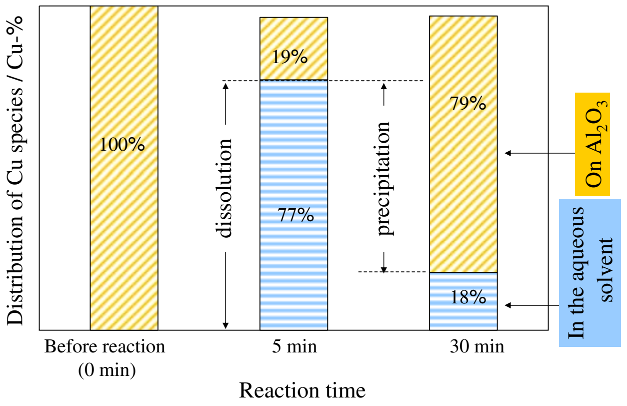

Fig. 4 Dissolution-precipitation behavior of Cu species during the reaction. Naphthalene, 10 mg; 1.0 M H_2O_2 aqueous solution, 10 mL; CuO/Al_2O_3, 20 mg; Reaction temperature, 100 °C

To clarify the dissolution-precipitation behavior of copper species supported on alumina, the solid catalyst were sampled at 5 min and 30 min of the reaction time, and the copper distribution was determined in an aqueous solution or on alumina support (Fig. 4). At 5 min, about 80% of Cu species were dissolved into the solution. At 30 min, the copper ions in the solution decreased to 18% and the 79% of Cu species were on the catalyst support, which implied that about 60% of Cu species was precipitated onto the support during the reaction. Total amount of copper distribution was less than 100% because of the determination error in the analysis by AAS. The concentrations of copper ions in aqueous media were decreased with the increasing pH value (Fig. 3). Copper species are dissolved into the solution by the intermediate organic acids and precipitated with increasing pH toward neutral in the reaction proceed. Initial formation of organic acid was formed on the solid copper oxides because initially almost all copper species were fixed on the catalyst support. But copper ions also have catalytic activity. At least the oxidations of WSOCs would be catalyzed on both heterogeneous copper species on the support and homogeneous copper ions in the solution.

Effect of support materials on the naphthalene oxidation

Table 2 shows the conversions of naphthalene and hydrogen peroxide, yield of WSOCs, and leaching of Cu species in the wet oxidation with hydrogen peroxide at 100 °C over copper oxide on various kinds of catalyst supports.

Table 2 The catalytic wet oxidation of naphthalene over copper oxide supported on various catalyst supports at 100 °C

Catalyst supports	Conversion/%		Yield/C-%	Cu/ppm
	Naphthalen	H_2O_2	WSOCs	
Blank	11.5	2.0	17.7	n.d.
Al_2O_3	100	100	2.7	17.9
TiO_2	100	100	5.7	42.8
SiO_2	100	100	8.3	51.2
Activated carbon	100	100	2.2	16.5
CeO_2	54.3	100	25.6	5.7
MnO_2	18.6	100	5.0	0.3

Catalyst, 20 mg; Naphthalene, 10 mg; 1.0 mol L^{-1} H_2O_2, 10 mL; Reaction time, 30 min

CuO/MnO_2 and CuO/CeO_2 catalysts showed low conversion of naphthalene, which would be due to the preferential consumption of hydrogen peroxide by the support materials. Over CuO/TiO_2 and CuO/SiO_2 catalysts, naphthalene was completely converted. However, much of the intermediate WSOCs remained in the aqueous solution, and the elution of copper was 43 ppm and 52 ppm. Over CuO/AC and CuO/Al_2O_3 catalysts, naphthalene was completely converted and the yields of intermediate WSOCs were found to be low at 2.2 C-% (21 ppm-C) and 2.7 C-% (25 ppm-C), and the elution of copper ions was also low at 17 ppm and 18 ppm. The concentrations less than 20 ppm of leaching copper ion were similar to or relative by lower than the other reports [12, 26]. In conclusion, active carbon and alumina were appropriate catalytic supports of copper oxide for the wet oxidation with hydrogen peroxide. However, some parts of Cu species were dissolved with intermediate organic acids formed during the reaction.

The successive batch reaction

As shown in Figs. 3 and 4, Cu species was dissolved by organic acids formed during the reaction, and the elution of copper ions was suppressed with the increase of pH toward neutral in the solution. To clarify the catalytic activity of the precipitated Cu species on alumina, the successive batch reactions were done at 100 °C for 30 min with the same catalyst (Fig. 5). The supernatant solution was removed by a centrifugal separation after the reaction (curve (a)). And then, fresh naphthalene and hydrogen peroxide solution were added and the temperature increased to 100 °C. After the first reaction, about 50% of Cu species was precipitated on alumina support as blue carbonate salt (Fig. 4). Introducing fresh hydrogen peroxide with naphthalene in the second reaction, the catalyst changed in color to dark gray, which might be due to the formation of copper oxide. However, about 20% of initial copper species was dissolved in every run. Furthermore, the pH was decreased with the increase of the remained organic acids because the activity of catalyst decreased with each run. Therefore, the catalytic activity decreased markedly as curve (a) in Fig. 5.

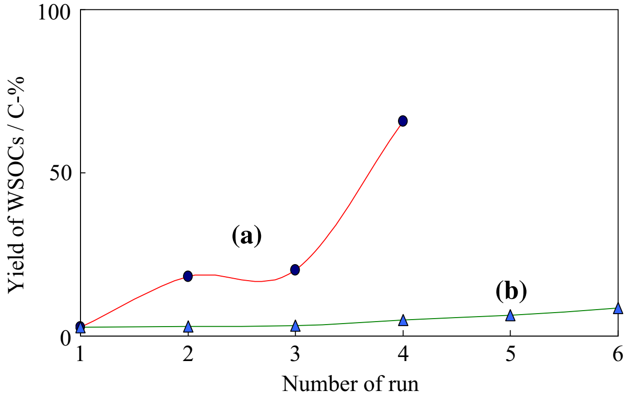

Fig. 5 Successive batch reaction at 100 °C for 30 min. After each reaction run, the catalyst was removed by a centrifugal separation without (a) or with (b) Na_2CO_3. Naphthalene, 10 mg; 1.0 M H_2O_2 aqueous solution, 10 mL; Cu/Al_2O_3, 20 mg

To suppress the copper elution, sodium carbonate was added into the solution. When sodium carbonate was added into the solution before reaction, not only the elution of copper ions but also the catalytic activity of CuO/Al_2O_3 was suppressed (not shown data) probably because of the high pH of solution, which corresponded to references [27, 28]. Therefore, sodium carbonate was added into the solution after every reaction (curve (b) in Fig. 5). And then, after the centrifugal washing with distilled deionized water, the catalyst was used as the nest reaction. The elution of copper species was suppressed to be less than 2 ppm. In the second reaction, the naphthalene was completely converted and the yield of WSOCs was 3.2 C-%. The copper species precipitated with Na_2CO_3 showed almost the same catalytic activity as that of the fresh CuO/Al_2O_3 catalyst. The complete conversion of naphthalene and the deep removal of WSOCs was done in the six successive reactions. However, the concentration of remained WSOCs increased little by little with the number of runs, which may be due to coking of WSOCs and their derivatives like deactivations of novel metal catalysts in wet oxidations [29, 30].

Conclusions

In the catalytic wet oxidation with hydrogen peroxide, naphthalene is oxidized at a temperature more than 50 °C. CuO catalysts supported on alumina and active carbon show a high activity for oxidation.

Copper species is dissolved by the low pH solution containing intermediate organic acids. The copper ions are precipitated with the increase of pH toward neutral by the conversion of the organic acids. The precipitated copper species show the catalytic activity. However, the catalyst is deactivated by the elution of Cu species in the successive reactions.

The sodium carbonate treatment after the reaction resulted in the low elution of copper species less than 2 ppm and in the complete conversion of naphthalene and the deep removal of WSOCs in the six successive reactions.

References

1. Bottini AT, Roberts JD (1957) J Am Chem Soc 79:1458
2. Graebwl HP, Hagenmaier H (1998) Organohalogen Compd 36:21
3. Okuda K, Yanagisawa K, Moritaka S, Onda A, Kajiyoshi K (2003) Polym Degrad Stab 79:105
4. Mishra VS, Mahajani VV, Joshi JB (1995) Ind Eng Chem Res 134:2
5. Thornton TD, Savage PE (1992) Ind Eng Chem Res 31:2451
6. Sadana A, Katzer JR (1974) J Catal 35:140
7. Pintar A, Levec J (1992) J Catal 135:345
8. Vaidya PD, Mahajani VV (2002) Adv Environ Res 6:429
9. Jin FM, Kishita A, Moriya T, Enomoto H (2001) J Supercrit Fluid 19:251
10. Shende RV, Levec J (2000) Ind Eng Chem Res 39:40
11. Matatov-Meytal YI, Shwintuch M (1998) Ind Eng Chem Res 37:309
12. Santos A, Yustos P, Quintanilla A, Ruiz G, Garcia-Ochoa F (2005) Appl Catal B: Environ 61:323
13. Guo J, Al-Dahhan M (2003) Ind Eng Chem Res 42:2450
14. Katzer JR (1978) Ind Eng Chem Fund 17:234
15. Santos A, Yustos P, Quintanilla A, Garcia-Ochoa F, Casas JA, Rordriguez JJ (2004) Environ Sci Technol 28:133
16. Furusawa T, Tsutsumi A (2004) Appl Catal A 278:207
17. Zhao H, Draelants DJ, Baron GV (2000) Ind Eng Chem Res 39:3195
18. Zhang XW, Shen SC, Yu LE, Kawi S, Hidajat K, Simon Ng KY (2003) Appl Catal A 250:341
19. Shie JL, Chang CY, Chen JH, Tsai WT, Chen YH, Chiou CS, Chang CF (2005) Appl Catal B: Environ 58:289
20. Carno J, Ferrandon M, Bjornbom E, Jaras S (1997) Appl Catal A 155:265
21. Vostrikov AA, Dubov DY, Psarov SA (2001) Russ Chem Bull, Int Ed 50:1481
22. Chen YH, Chang CY, Huang SF, Chiu CY, Ji D, Shang NC, Yu YH, Chiang PC, Ku Y, Chen JN (2002) Water Res 36:4144
23. Legube B, Guyon S, Sugimitsu H, Dore M (1986) Water Res 20:197
24. Hefter GT (1989) Solubility data series, vol 38 (Hydrocarbons Water Seawater, Pt. 2), pp 236–249
25. Onda A, Suzuki Y, Kajiyoshi K, Yanagisawa K (2006) Ind Eng Chem Res 45:2194
26. Sotelo JL, Ovejero G, Martinez F, Melero JA, Milieni A (2004) Appl Catal B: Environ 47:281
27. Plgnatello JJ (1992) Environ Sci Technol 26:944
28. Ramirez JH, Costa CA, Madeira LM, Mata G, Vicente MA, Rojas-Cervantes ML, López-Peinado AJ, Martín-Aranda RM (2007) Appl Catal B: Environ 71:44
29. Hamoudi S, Sayari A, Belkacemi K, Bonneviot L, Larachi F (2000) Catal Today 62:379
30. Masende ZPG, Kuster BFM, Ptasinski KJ, Janssen FJJG, Katima JHY, Schouten JC (2003) Appl Catal B: Environ 41:247