

REFERENCES

- Adesina, A. A., Hudgins, R. R. and Silveston, P. L. Fischer-Tropsch synthesis under periodic operation. *Catal. Today*, 25 (1995): 127-144.
- Aida, T. and Kawakami, R. Periodic operation effects in selective catalytic reduction of nitrogen monoxide with propane over alumina. *J. Chem. Eng. Japan*, 30 (1997): 321-327.
- Amato, G., Arcoria, A., Ballistreri, F. P., Tomaselli, G. A., Bortolini, O., Conte, V., Di Furia, F., Modena, G. and Valle, G. Oxidations with peroxotungsten complexes: rates and mechanism of stoichiometric olefin epoxidations. *J. Mol. Cat.*, 37 (1986): 165-175.
- Bengoa, J. F., Gallegos, N. G., Marchetti, S. G., Alvarez, A. M., Cagnoli, M. V. and Yeramia'n, A. A. Influence of TS-1 structural properties and operation conditions on benzene catalytic oxidation with H₂O₂. *Micropor. Mesopor. Mater.*, 24 (1998): 163-172.
- Bhaumik, A., Mukherjee, P. and Kumar, R. Triphase catalysis over titanium-silicalite molecular sieves under solvent-free conditions. *J. Catal.*, 178 (1998): 101-107.
- Boelhouwer, J. G., Piepers, H. W. and Drinkenburg, A. A. H. The induction of pulses in trickle-bed reactors by cycling the liquid feed. *Chem. Eng. Sci.*, 56 (2001): 2605-2614.
- Bolis, V., Bordiga, S., Lamberti, C., Zecchina, A., Carati, A., Rivetti, C., Spano, G. and Petrini, G. A calorimetric, IR, XANES and EXAFS study of the adsorption of NH₃ on Ti-silicalite as a function of the sample pre-treatment. *Micropor. Mesopor. Mater.*, 30 (1999): 67-76.
- Carlsson, P.A., Mollner, S., Arnby, K. and Skoglundh, M. Effect of periodic operation on the low-temperature activity for propane oxidation over Pt/Al₂O₃ catalysts. *Chem. Eng. Sci.*, 59 (2004): 4313-4323.
- Clerici, M. G. and Ingallina, P. Oxidation reactions with in situ generated oxidants. *Catal. Today*, 41 (1998): 351-364.
- Hulea, V. and Dumitriu, E. Styrene oxidation with H₂O₂ over Ti-containing molecular sieves with MFI, BEA and MCM-41 topologies. *Appl. Catal.*, 277 (2004): 99-106.
- Haure, R. M., Hudgins, R. R. and Silveston, P. L. Periodic operation of a trickle-bed reactor. *Alche J.*, 35 (1989) 1437-1444.

- Gulari, E., Zhou, X. and Sxe, C. Catalytic oxidation of carbon monoxide under periodic and transient operation. *Catal. Today*, 25 (1995): 145-157.
- Kong, L., Li, G. and Wang, X. Mild oxidation of thiophene over TS-1/H₂O₂. *Catal. Today*, 93-95 (2004): 341-345.
- Khouw, C. B., Dartt, C. B., Labinger, J. A. and Davis, M. E. Studies on the Catalytic-Oxidation of Alkanes and Alkenes by Titanium Silicates. *J. Catal.*, 149 (1994): 195-205.
- Kraushaar-Czarnetzki, B. and Van Hooff, J.H.C. A test reaction for titanium silicalite catalysts. *Catal. Lett.*, 2 (1988): 43-48.
- Kumar, R., Mukherjee, P. and Bhaumik, A. Enhancement in the reaction rates in the hydroxylation of aromatics over TS-1/H₂O₂ under solvent-free triphase conditions. *Catal. Today*, 49 (1999): 85-191.
- Li, G., Wang, X., Guo, X., Liu, S., Zhao, Q., Bao, X. and Lin, L. Titanium species in titanium silicalite TS-1 prepared by hydrothermal method. *Mater. Chem. Phys*, 71 (2001): 195-201.
- Liu, H., Lu, G., Guo, Y., Guo, Y. and Wang, J. Effect of pretreatment on properties of TS-1/diatomite catalyst for hydroxylation of phenol by H₂O₂ in fixed-bed reactor. *Catal. Today*, 93-95 (2004): 353-357.
- Liu, H. Lu, G., Guo Y., Guo Y. and Wang J. Deactivation and regeneration of TS-1/diatomite catalyst for hydroxylation of phenol in fixed-bed reactor. *J. Chem. Eng.*, 108 (2005): 187-192.
- Martens, J.A., Buskens, Ph., Jacobs, P.A., Van der Pol, A., Van Hooff, J.H.C., Ferrini, C., Kouwenhoven, H.W., Kooyman, P.J. and Van Bekkum, H. Hydroxylation of phenol with hydrogen peroxide on EUROTTS-1 catalyst. *Appl. Catal. A*, 99 (1993): 71-84.
- Massa, P., Ayrde, M.A., Ivorra, F., Fenoglio, R. and Haure, P. Phenol oxidation in a periodically operated trickle bed reactor. *Catal. Today*, 107-108 (2005) 630-636.
- Notari, B. Synthesis and catalytic properties of titanium containing zeolites. *Stud. Surf. Sci. Catal.*, 37 (1989): 413-425.
- Pirutko, L.V., Uriarte, A.K., Chernyavsky, V.S. and Kharitonov, A.S. Preparation and catalytic study of metal modified TS-1 in the oxidation of benzene to phenol by N₂O. *Micropor. Mesopor. Mater.*, 48 (2001): 345-353.

- Romano, U., Esposito, A., Maspero, F., Neri, C. and Clerici, M. G., *Chim. Ind. (Milan)*, 72 (1990): 610.
- Sheldon, R. A. and Van Bekkum, H. Reactors, *Fine Chemicals through Heterogeneous Catalysis.*, (2001): 45-60.
- Silveston, P. L., Hudgins, R. R. and Renken, A. Periodic operation of catalytic reactors-introduction and overview. *Catal. Today*, 25 (1995): 91-112.
- Stradiotto, D. A., Hudgins, R. R. and Silveston, P. L. Hydrogenation of crotonaldehyde under periodic flow interruption in a trickle bed. *Chem. Eng. Sci.*, 54 (1999): 2561-2568.
- Taramasso, M., Perego, G. and Notari, B., *US Patent*, 1983, 4410501.
- Tatsumi, T., Yuasa, K. and Tominaga, H. Hydroxylation of benzene and hexane by oxygen and hydrogen over palladium-containing titanium silicates. *J. Chem. Commun.*, 19 (1992): 1446-1447.
- Tendulkar, S.B., Tambe, S.S., Chandra, I., Rao, P.V., Naik, R.V. and Kulkarni, B.D., Hydroxylation of phenol to dihydroxybenzenes: development of artificial neural-network-based process identification and model predictive control strategies for a pilot plant scale reactor. *Ind. Eng. Chem. Res.*, 37 (1998): 2081-2085.
- Thangaraj, A., Kumar, R. and Ratnasamy, P. Direct catalytic hydroxylation of benzene with hydrogen peroxide over titanium-silicalite zeolites. *Appl. Catal. A.*, 57 (1990): L1-L3.
- Turco, F., Hudgins, R. R., Silveston, P. L., Sicardi, S., Manna, L. and Banchemo, M. Investigation of periodic operation of a trickle-bed reactor. *Chem. Eng. Sci.*, 56 (2001): 1429-1434.
- Van der Pol, A.J.H.P. and Van Hooff, J.H.C. Parameters affecting the synthesis of titanium silicalite-1. *Appl. Catal. A*, 92 (1992): 93-111.
- Weitkamp, J., Ermst, S., Roland, E. and Thiele, G. F. The modified hydrophobicity index as a novel method for characterizing the surface properties of titanium silicalites. *Stud. Surf. Sci. Catal.*, 105 (1997): 763-770.
- Yamada, H. and Goto, S. periodic operation of trickle bed reactor for hydrogenolysis in gas-liquid-liquid-solid four phases. *J. Chem. Eng. Japan*, 30 (1997): 478-483.

Zecchina, A., Spoto, G., Bordiga, S. Padovan, M. and Leofanti, G. Catalysis and absorption by zeolites. Pfeifer, H. and Fricke(EDS.), R. Proceedings of the ZEOCAT 90, Leipzig, 20-30 August, 1990. *Stud. Surf. Sci. Catal.*, 30 (1991): 67.

APPENDICES

APPENDIX A

CALCULATION FOR CATALYST PREPARATION

Calculation of Si/Ti Atomic Ratio for TS-1

The calculation is based on weight of Sodium Silicalite ($\text{Na}_2\text{O}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$) in B1 and B2 solutions (Topic 4.1.2).

$$\text{Molecular Weight of Si} = 28.0855$$

$$\text{Molecular Weight of SiO}_2 = 60.0843$$

$$\text{Weight percent of SiO}_2 \text{ in sodium Silicate} = 28.5$$

Using Sodium Silicate 69 g with 45 g of water as B1 solution.

$$\begin{aligned} \text{mole of Si used} &= \text{wt.} \times \frac{(\%)}{100} \times \frac{(\text{M.W. of Si})}{(\text{M.W. of SiO}_2)} \times \frac{(1 \text{ mole})}{(\text{M.W. of Si})} \\ &= 69 \times (28.5/100) \times (1/60.0843) \\ &= 0.3273 \end{aligned}$$

For example, to prepare TS-1 at Si/Ti atomic ratio of 32 by using $\text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$ for Ti source.

$$\text{Molecular Weight of Ti} = 47.88$$

$$\text{Molecular Weight of Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4 = 340.36$$

$$\text{Weight percent purity of Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4 = 97$$

Si/Ti atomic ratio = 32

$$\begin{aligned} \text{mole of Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4 \text{ required} &= 0.3273/32 \\ &= 1.02 \times 10^{-2} \text{ mole} \\ \text{amount of Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4 &= 1.02 \times 10^{-2} \times 340.36 (100/97) \\ &= 3.5889 \text{ g} \end{aligned}$$

which used in A1 and A2 solutions.

APPENDIX B

DATA AND CALCULATION OF ACID SITE

Table B1 Reported total peak area from Micromeritics Chemisorb 2750

Sample No.	Reported total peak area
1	0.0392
2	0.0405
3	0.0425
4	0.0403
5	0.0153
6	0.0211
7	0.0288
8	0.0234
9	0.0159

Calculation of total acid sites

For example, sample No.1, total acid site is calculated from the following step.

1. Conversion of total peak area to peak volume

conversion from Micromeritics Chemisorb 2750 is equal to 77.5016 ml/area unit. Therefore, total peak volume is derived from

$$\begin{aligned}\text{Total peak volume} &= 77.5016 \times \text{total peak area} \\ &= 77.5016 \times 0.0392 \\ &= 3.0411 \text{ ml}\end{aligned}$$

2. Calculation for adsorbed volume of 15% NH₃

$$\begin{aligned}
 \text{adsorbed volume of 15\% NH}_3 &= 0.15 \times \text{total peak volume} \\
 &= 0.15 \times 3.0411 \text{ ml} \\
 &= 0.4562 \text{ ml}
 \end{aligned}$$

3. Total acid sites are calculated from the following equation

$$\text{Total acid sites} = \frac{(\text{Adsorbed volume, ml}) \times 101.325 \text{ Pa}}{\left(8.314 \times 10^{-3} \frac{\text{Pa} \cdot \text{ml}}{\text{K} \cdot \mu\text{mol}}\right) \times 298 \text{ K} \times (\text{weight of catalyst, g})}$$

For sample No.2, 0.1009 g of this sample was measured, therefore

$$\begin{aligned}
 \text{Total acid sites} &= \frac{0.4562 \text{ ml} \times 101.325 \text{ Pa}}{\left(8.314 \times 10^{-3} \frac{\text{Pa} \cdot \text{ml}}{\text{K} \cdot \mu\text{mol}}\right) \times 298 \text{ K} \times (0.1000 \text{ g})} \\
 &= 186.55 \mu\text{mol H}^+/\text{g}
 \end{aligned}$$

Calculation of acid site ratio

As known, the first peak from desorption is indicated as weak acid, relative with another peak and the second one is strong acid. Ratio of each acid site on catalyst surface is calculated from reported peak area of peak fitting program as shown above.

For example, sample No.1, the ratio of each acid site on catalyst surface is calculated from the following equation.

$$\text{The ratio of weak acid} = \frac{1^{\text{st}} \text{ peak area}}{\text{summation of both peak areas}} \times 100 \%$$

From Fig. 5.13., 1st peak area and 2nd peak area are equal to 0.0482 and 0.0332, respectively.

$$\begin{aligned}\text{The ratio of weak acid} &= \frac{0.0482}{0.0482 + 0.0332} \times 100 \% \\ &= 59.21 \%\end{aligned}$$

$$\begin{aligned}\text{therefore, the ratio of strong acid} &= 100 - 59.21 \% \\ &= 40.79 \%\end{aligned}$$

APPENDIX C

CALIBRATION CURVES

This appendix shows the calibration curves for calculation of composition of reactant and products in hydroxylation of benzene reaction. The reactant is benzene and the main product is phenol.

The flame ionization detector, gas chromatography Shimadzu model 9A was used to analyze the concentration of benzene and phenol by using GP 10% SP-2100 column.

Mole of reagent in y-axis and area reported by gas chromatography in x-axis are exhibited in the curves. The calibration curves of benzene and phenol are illustrated in the following figures.

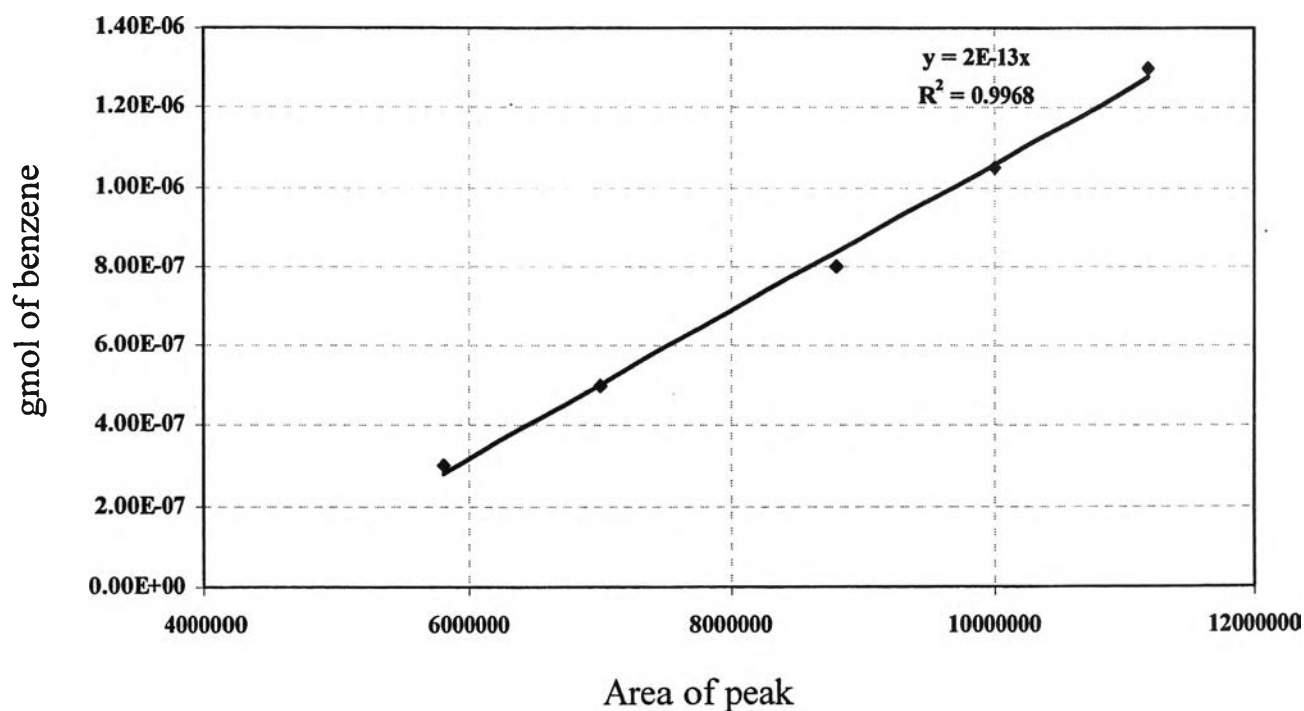


Figure C.1 The calibration curve of benzene.

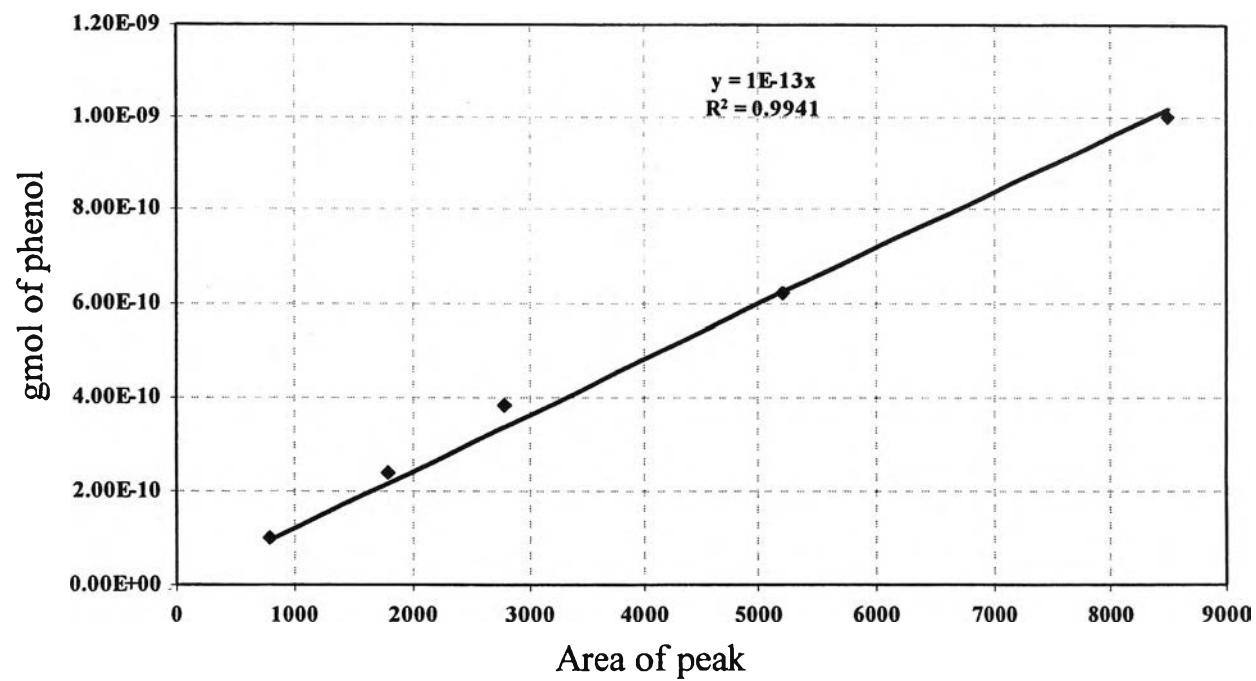


Figure C.2 The calibration curve of phenol.

APPENDIX D

CALCULATION OF BENZENE CONVERSION

The catalyst performance for the hydroxylation of benzene was evaluated in terms of activity for benzene conversion.

Activity of the catalyst performed in term of benzene conversion. Benzene conversion is defined as overall mole of phenol during the cycle period with respect to overall mole of benzene in feed passed through reactor during the cycle period.

$$\text{benzene conversion (\%)} = 100 \times \frac{\text{overall mole of phenol during cycle period}}{\text{overall mole of benzene passed through reactor during cycle period}} \quad (\text{D1})$$

where mole of phenol can be measured employing the calibration curve of phenol in Figure C.2, Appendix C., i.e.,

$$\text{mole of phenol} = ((\text{area of phenol peak from integrator plot on GC-9A}) \times 1 \times 10^{-13}) \quad (\text{D2})$$

where mole of benzene can be measured employing the calibration curve of benzene in Figure C.1, Appendix C., i.e.,

$$\text{mole of benzene} = ((\text{area of phenol peak from integrator plot on GC-9A}) \times 2 \times 10^{-13}) \quad (\text{D3})$$

APPENDIX E

DATA OF EXPERIMENTS



Table E1 Data of Figure 5.21

Reaction time (min)	Benzene conversion (%)			
	Si/Ti = 60	Si/Ti = 40	Si/Ti = 32	Si/Ti = 22
30	0.0029	0.002	0.0012	
75			0.0024	0.0029
90	0.0053	0.0041		
105	0.0078	0.0055	0.0088	
120	0.0111	0.012		0.0081
150		0.0208	0.0179	
165		0.0464	0.0363	0.0176
195		0.053		0.0259
210				0.0281
225	0.0097	0.0519		
240			0.1175	0.0337
285	0.0114	0.1079		0.0288
315			0.1383	
330			0.1272	
390			0.1385	0.0181
435	0.0077		0.1706	0.03
480	0.0199	0.1593	0.1633	0.0211
555	0.0092		0.1586	
570			0.1699	0.0373
600	0.0137	0.2299	0.1641	

Table E2 Data of Figure 5.22

Reaction time (min)	Benzene conversion (%)		
	unpretreatment	pretreatment with HNO ₃	
		3 molar	5 molar
30	0.002	0.0658	0.0998
75		0.0468	0.1382
90	0.0041		0.1036
105	0.0055		0.1181
120	0.012		0.1279
150	0.0208		0.1277
165	0.0464		0.1102
195	0.053		0.1195
225	0.0519	0.098	0.1173
240			0.0932
285	0.1079	0.1036	0.1294
315		0.1045	0.1157
330		0.1141	
390		0.1099	0.1407
435		0.1251	0.1494
480	0.1593	0.1667	
555		0.1623	
570		0.1699	0.2151
600	0.2299	0.2114	0.2251

Table E3 Data of Figure 5.23

Reaction time (min)	Benzene conversion (%)	
	unpretreatment	pretreatment with 5M HNO ₃
30	0.0029	0.0238
75		0.029
90	0.0053	
105	0.0078	
120	0.0111	
150		0.0284
165		0.02
210		0.0198
225	0.0097	0.0204
240		
285	0.0114	0.0302
315		0.0279
390		0.0128
435	0.0077	
480	0.0199	0.0283
555	0.0092	0.0144
600	0.0137	0.0217

Table E4 Data of Figure 5.24

Reaction time (min)	Benzene conversion (%)	
	unpretreatment	pretreatment with 5M HNO ₃
30	0.0012	0.0653
75	0.0024	0.1409
105	0.0088	
120		0.2305
150	0.0179	
165	0.0363	
240	0.1175	0.2855
285		0.2597
315	0.1383	
330	0.1272	
390	0.1385	0.1495
435	0.1706	0.1485
480	0.1633	0.2458
555	0.1586	0.182
570	0.1699	0.0944
600	0.1641	0.1014

Table E5 Data of Figure 5.25

Reaction time (min)	Benzene conversion (%)	
	unpretreatment	pretreatment with 5M HNO ₃
30		0.0422
75	0.0029	0.0757
105		0.2305
120	0.0081	0.075
165	0.0176	0.1216
195	0.0259	0.0957
210	0.0281	0.0743
240	0.0337	0.0979
285	0.0288	
390	0.0181	0.0705
435	0.03	0.0813
480	0.0211	0.049
570	0.0373	0.1143
600		0.1149

APPENDIX F

MATERIAL SAFETY DATA SHEET OF BENZENE AND HYDROGENPEROXIDE

Benzene

Safety data for benzene

General

Synonyms: benzol, phenyl hydride, coal naphtha

Molecular formula: C₆H₆

Physical data

Appearance: colourless liquid

Melting point: 5.5 °C

Boiling point: 80 °C

Specific gravity: 0.87

Vapour pressure: 74.6 mm Hg at 20 °C

Flash point: -11 °C

Explosion limits: 1.3 % - 8 %

Autoignition temperature: 561 °C

Stability

Stable. Substances to be avoided include strong oxidizing agents, sulphuric acid, nitric acid. Highly flammable.

Toxicology

This material is a known carcinogen. The risks of using it in the laboratory must be fully assessed before work begins. TLV 10 ppm. Short-term exposure may cause a variety of effects, including nausea, vomiting, dizziness, narcosis, reduction in blood pressure, CNS depression. Skin contact may lead to dermatitis. Long-term exposure may lead to irreversible effects. Severe eye irritant. Skin and respiratory irritant.

Personal protection

Safety glasses, gloves, good ventilation. Thought should be given to using an alternative, safer product.

Hydrogen Peroxide, 30% solution

Safety data for hydrogen peroxide, 30% solution

General

Synonyms: albone 30, albone 35, albone 50, albone 70, albone 35cg, albone 50cg, albone 70cg, interox, kastone, perone 30, perone 35, perone 50. Data also applies to solutions of similar strength.

Note: Typical concentrations lie in the range 3%-35%. Solutions of much higher concentration (e.g. 60% and above) present significantly increased risks, and should not be used unless such strength is absolutely essential.

Physical data

Appearance: colourless liquid

Melting point: ca. -28 °C

Boiling point: ca. 114 °C

Specific gravity: typically near 1.19

Vapour pressure: 23.3 at 30 °C

Stability

Unstable - readily decomposes to water and oxygen. Light sensitive. May develop pressure in the bottle - take care when opening. Forms potentially explosive compounds with ketones, ethers, alcohols, hydrazine, glycerine, aniline, sodium borate, urea, sodium carbonate, triethylamine, sodium fluoride, sodium pyrophosphate and carboxylic acid anhydrides. Materials to avoid include combustibles, strong reducing agents, most common metals, organic materials, metallic salts, alkali, porous materials, especially wood, asbestos, soil, rust, strong oxidizing agents.

Toxicology

Toxic. Corrosive - can causes serious burns. Eye contact can cause serious injury, possibly blindness. Harmful by inhalation, ingestion and skin contact. Typical OEL 1 ppm.

Personal protection

Safety glasses are essential; acid-resistant gloves are suggested. Suitable ventilation.

VITA

Miss Pareeyanun Kamonsawat was born on February 3rd 1981 in Bangkok, Thailand. She finished high school from Satreesamupakarn School, Samutprakarn in 1999, and received the bachelor's degree of Chemistry from Faculty of Science, Mahidol University in 2003. She continued her master's degree of Chemical Engineering at Chulalongkorn University in October, 2006.

