NOTE

ALUM MUD: PHASE IDENTIFICATION AND CATALYTIC POTENTIAL FOR AQUEOUS-PHASE DECOMPOSITION OF HYDROGEN PEROXIDE

AMIT ADAK, DURJOY MALLIK, SWAPAN KHANRA, AND SWADES K. CHAUDHURI[†]

Department of Chemical Engineering, University of Calcutta 92, A.P.C. Road, Calcutta-700009, India

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INTRODUCTION

Alum mud (AM), a solid residue, is generated during the manufacture of alum from bauxite ore by digesting with H_2SO_4. Because of the use of different bauxite ores and different operating conditions, the chemical and mineralogical composition of AM varies. In general, AM can be characterized as an acidic slurry of very fine particles of aluminum oxide, iron oxide, silica, titanium dioxide, *etc.* and/or a mineralogy of different phases like biotite, mullite, quartz, hematite, rutile, *etc.* The disposal of high volume-solid-wastes like AM, red mud, and fly ash is currently a pressing issue. With the amount of landfill space declining, utilization as a form of disposal is quickly becoming a necessity rather than a choice. Many research groups are working on various productive-use applications of such solid wastes. Though considerable work was done both on fly ash and red mud (Klopries *et al.,* 1990; Emasiri *et al.,* 1992; Daniels *et al.,* 1993; Weng and Hung, 1994; Batabyal *et al.,* 1995; Sur *et al.,* 1996), very little attention was given to AM.

Hydrogen peroxide, an eco-friendly oxidant, was used for years in waste treatment to detoxify a wide range of aqueous and gaseous pollutants in the presence of various catalysts (Borup and Ashcroff, 1992; Murakoshi *et al.,* 1992; Lother and Walton, 1993) which are generally present in AM, fly ash, and red mud. The use of mineral-catalyzed peroxide treatment based on H_2O_2 has recently received increased attention in remediation of contaminated soil containing various chlorinated compounds, pesticides, *etc.* where bioremediation may not be effective for high biorefractory contaminants (Watts *et al.,* 1990; Tyre *et al.,*

1991; Gates and Siegrist, 1995; Watts *et al.,* 1997) and in ground water treatment (Clancy *et al.,* 1996). The decomposition of H_2O_2 to provide an active oxidant, either hydroxyl radical or nascent oxygen for the oxidative degradation of contaminants, depends on the pH of the medium; low pH favors the formation of a hydroxyl radical (Tyre *et al.,* 1991) and high pH decomposes H_2O_2 to water and nascent oxygen (Khan and Watts, 1996). Christopher and Chattopadhyay (1993) disclosed a SiO_2 catalyzed peroxide treatment process for detoxifying wastewater containing cyanide and other pollutants in alkaline media in the temperature range of 283–383 K using H_2O_2. Some investigators (Romano *et al.,* 1990, Thangaraj *et al.,* 1991; Castillo *et al.,* 1996) also reported the catalytic activity of mineral phases, such as titanium-silicates, in the hydroxylation of phenols with H_2O_2. Recently, Sur *et al.* (1996) and Mallik *et al.* (1997) reported the catalytic potential of mineral phases of coal fly ash in peroxidative decolorization of aqueous dye solutions and aqueous sodium sulfide solutions, respectively. Most of the mineral phases used in the decomposition of H_2O_2 in the treatment of hazardous wastes are also present in AM. Thus, AM seems to be an effective heterogeneous catalyst for the decomposition of H_2O_2 in the course of peroxidative treatment of various hazardous effluents such as organophosphate pesticide containing effluent, colored dye effluent, sulfide-bearing effluents, *etc.* and as an auto-catalyst in H_2O_2 based remediation of contaminated sites containing disposed AM. Here, we report preliminary findings on the catalytic potential of AM for aqueous phase decomposition of H_2O_2 in an alkaline medium.

MATERIALS AND METHODS

AM was obtained from M/S Bengal Chemicals and Pharmaceutical Ltd., West Bengal, India. Before use, the highly acidic mud was washed several times with

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[†] Present address: Visiting Scientist, Department of Mining and Mineral Resources Engineering, Southern Illinois University at Carbondale, Carbondale, Illinois 62901.
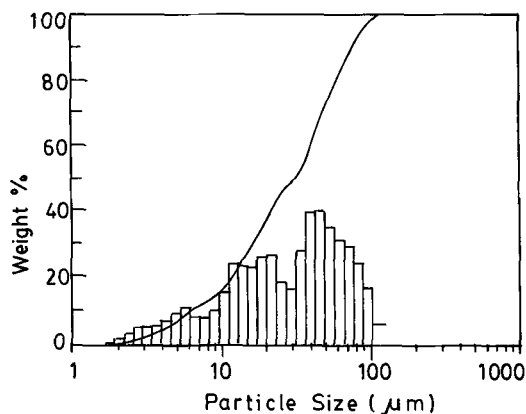
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Figure 1.   Particle size distribution of alum mud used as catalyst.

Figure 2.   SEM of alum mud particles used as catalyst.

distilled water until the pH of the wash water increased to 6.0 ± 0.2. The washed mud was dried at $105 \pm 5°C$ in nitrogen atmosphere for 8 h, cooled to ambient temperature, and used in the experiments described below. Analytical grade H_2O_2 [30% weight/volume (w/v)] was used for experiments and dilutions were made as required.

Particle size analysis of AM involved a laser particle size analyzer (Malvern Instruments, Model M 7.06) using isoamyl alcohol as a solvent. An X-ray diffraction (XRD) pattern of AM was obtained with a Philips Analytical X-ray Diffractometer (Model PW 1710) using Ni-filtered CuKα radiation. Scanning Electron Microscopy (SEM) using a Cam Scan (Model 2DV) instrument with Energy Dispersive X-ray Spectrophotometry (EDX) capabilities was used.

The decomposition reaction of H_2O_2 was studied in a 9.5×10^{-2} m inside diameter fully baffled, mechanically agitated batch reactor constructed of glass, and equipped with a six-blade glass disc-turbine impeller (diameter 3.0×10^{-2} m). The reactor was immersed in a constant temperature water bath where temperature was controlled within $\pm 1°C$. For each procedure, 0.20 l of distilled water was placed in the reactor and allowed to reach the desired reaction temperature. Then, H_2O_2 solution (30% w/v) was added to the reactor and agitated for a few seconds to make a homogeneous mixture. Then, a known quantity of dried AM was added to the reactor, and the mixture was again agitated at a controlled speed. Samples were withdrawn from the reaction product at regular intervals of 15 min after stopping the agitation for few seconds to allow the AM particles to settle. The concentration of undecomposed H_2O_2 in the product was determined by the iodometric method (Vogel, 1978). Before the addition of AM to the reactor, a small volume of the product was withdrawn for estimation of the initial H_2O_2 concentration. The decomposition of H_2O_2 was also studied in the absence of AM. Some
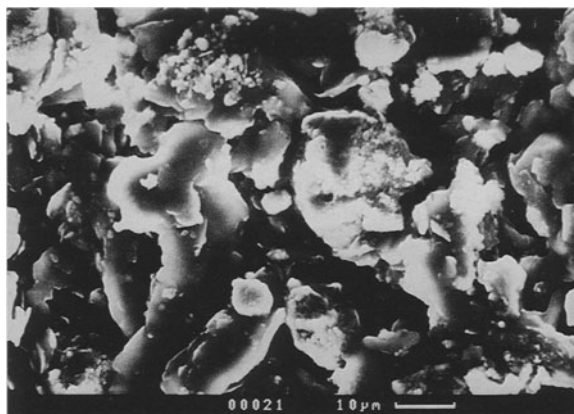
experiments with AM were repeated for replication purposes, and the average deviation was within $\pm 4.0\%$.

RESULTS AND DISCUSSION

Characterization of alum mud

The particle-size distribution of AM is shown in Figure 1. Weight percentage of different particle sizes in AM is represented in bars. SEM (Figure 2) analysis confirmed that the particle shape and morphology of AM varies. Figure 3 shows the elemental composition
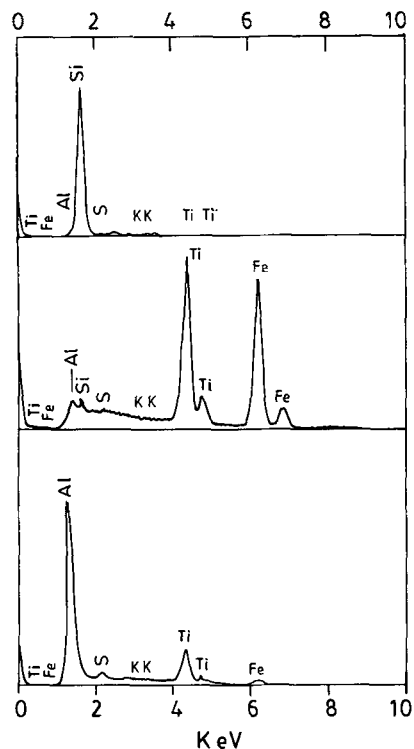

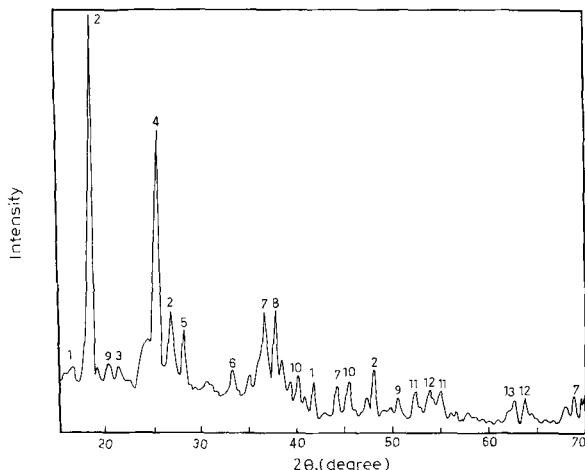Figure 3.   EDX of alum mud particles used as catalyst.

Figure 4. X-ray diffractogram of alum mud used as catalyst [1. Aluminium oxide (crystal structure not assigned); 2. Aluminium titanium oxide (orthorombic); 3. Sodium alumino silicate (cubic); 4. Aluminium oxide (monoclinic); 5. Gypsum (monoclinic); 6. Kyanite (triclinic); 7. Biotite (monoclinic); 8. Mullite (orthorhombic); 9. Quatrz (hexagonal); 10. Calcium aluminium oxyhydrate (crystal structure not assigned); 11. Rutile (tetragonal); 12. Hematite (rhombohedral); 13. Magnetite (cubic)].

of three different AM particles which also varies from particle to particle. Mineral phases were identified by comparing XRD patterns to the (inorganic) Powder Diffraction File (JCPDS International Center for Diffraction Data, 1989). Figure 4 displays the relatively sharp diffraction maximum associated with well-crystallized minerals like hematite, biotite, quartz, mullite, *etc.* The X-ray diffractographs of unwashed and water-washed AM are similar, therefore, washing has no apparent effect on the mineralogy of AM particles.

Decomposition of hydrogen peroxide

The accuracy of the experimental procedure was tested by performing experiments on decomposition of H_2O_2 without AM in distilled water (pH 6.8 ± 0.2). For an initial H_2O_2 concentration of 13.75×10^{-2} kmol m^{-3}, the experimental data correlated well with a first-order rate equation, $R = -dC/dt = kC$ (kmol m^{-3} s^{-1}), in the temperature range of 313–345 K (Table 1). The

Table 1. Nomenclature.

C	Concentration of hydrogen peroxide at any time t, kmol m^{-3}.
C_0	Initial concentration of hydrogen peroxide, kmol m^{-3}.
k	Specific first order rate constant for the decomposition of hydrogen peroxide, s^{-1}.
N	Speed of agitation, rev min^{-1}
R	Rate of decomposition of hydrogen peroxide, kmol m^{-3} S^{-1}.
t	Time, s.
W	Alum mud loading, %(w/v).

Table 2. Specific first order rate constants for decomposition of H_2O_2 under different conditions.

Temperature (K)	AM loading (% w/v)	pH of Reaction medium	Rate constant, k^1 (s^{-1})
313	—	5.65	3.72×10^{-7}
323	—	5.65	2.61×10^{-6}
333	—	5.65	1.30×10^{-5}
345	—	5.65	3.53×10^{-4}
313	—	9.24	3.75×10^{-5}
323	—	9.24	8.33×10^{-5}
333	—	9.24	16.63×10^{-5}
313	2.5	9.24	1.39×10^{-4}
313	5.0	9.24	2.59×10^{-4}
323	5.0	9.24	5.41×10^{-4}
333	5.0	9.24	11.90×10^{-4}
313	7.5	9.24	5.07×10^{-4}

[1] Calculated from the respective plot of $-\ln C/C_0$.

integral form of the rate equation, $-\ln C/C_0 = kt$, was used to calculate the rate-constants of the reaction. The first-order rate-constants obtained from the slopes of the plots of $-\ln C/C_0$ *vs.* t are reported in Table 2. An Arrhenius plot, based on the first-order rate-constants (Table 2) for decomposition of H_2O_2 without AM in distilled water, gave an apparent activation energy of 48.68 kcal mol^{-1}, which is in excellent agreement with the value of 50.0 kcal mol^{-1} (Kirk-Othmer, 1981).

Effect of temperature

Figure 5 shows the effect of temperature in the range of 313–333 K on decomposition of H_2O_2 with 5% (w/v) AM loading and without AM loading, at pH 9.24. In this temperature range, the first-order rate constant for decomposition is $\sim 7\times$ higher than where no
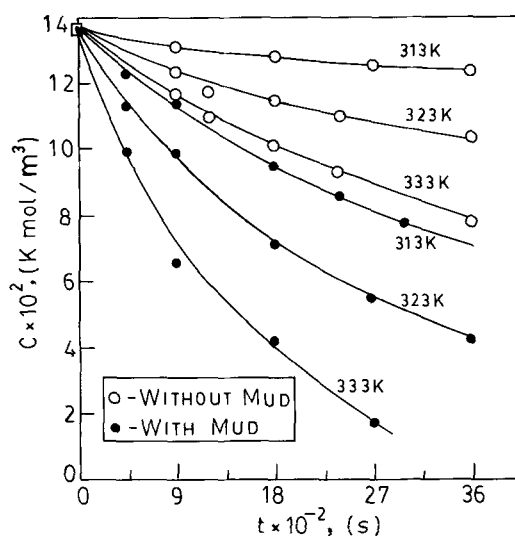

Figure 5. Effect of temperature on decomposition of H_2O_2 with and without alum mud (Operating conditions: V = 2.0 $\times 10^{-4}$ m^3; $C_0 = 13.75 \times 10^{-2}$ kmol m^{-3}; W = 5% (w/v); pH = 9.24; N = 850 rev min^{-1}; see Table 1).
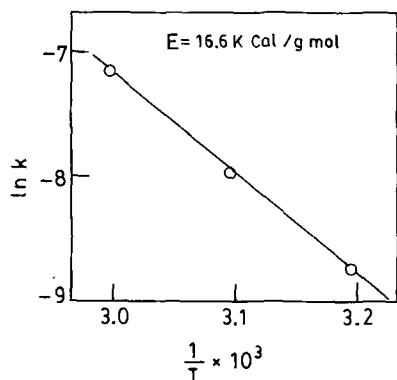
Figure 6.   Arrhenius plot for decomposition of H_2O_2 in presence of alum mud (Operating conditions: same as in Figure 5).

Figure 7.   Effect of alum mud loading on decomposition of H_2O_2 (Operating conditions: $V = 2.0 \times 10^{-4}$ m^3; $C_0 = 13.75 \times 10^{-2}$ kmol m^{-3}; $T = 313$ K; pH $= 9.24$; $N = 850$ rev min^{-1}).

AM is present under otherwise identical operating conditions (Table 2). An Arrhenius plot (Figure 6), based on the rate constants (Table 2), calculated from $-\ln C/C_0$ plots of respective C vs. t curves for 5% (w/v) AM loading (Figure 5) gave an apparent activation energy of 16.6 kcal mol^{-1}. It was also found that at 313 K, after the fifth repeated use of the same AM (batch time 1 h), the reduction of the catalytic effect of AM is 30% compared to that of fresh AM.

Effect of alum mud loading

Figure 7 shows the decomposition kinetics of H_2O_2 with AM in the range of 2.5–7.5% (w/v) loading. The extent of decomposition increases with increasing AM loading under otherwise identical operating conditions. The specific first-order rate-constants are reported in Table 2. The higher rate of decomposition of H_2O_2 with increasing AM loading suggests a surface reaction mechanism.

Effect of speed of agitation

Figure 8 shows that the speed of agitation in the range of 500–1600 rev min^{-1} has a nominal effect on the decomposition of H_2O_2 in the presence of 5% (w/v) AM loading at 313 K. However, above 1200 rev min^{-1}, the effect of the speed of agitation is nearly negligible. Therefore, mass transfer resistance can be neglected in this reaction in the range of 500–1600 rev min^{-1}.

Effect of pH

The effect of pH in the range of 7.56–11.58 was studied also at 313 K in the presence of 5% (w/v) AM loading. Figure 9 and Table 2 illustrate that pH has a significant effect on the decomposition of H_2O_2 in the presence as well as the absence of AM. The extent of decomposition of H_2O_2 increases with increasing pH in the range 7.56–11.58 in the presence of 5% (w/v) AM loading under otherwise identical operating conditions.
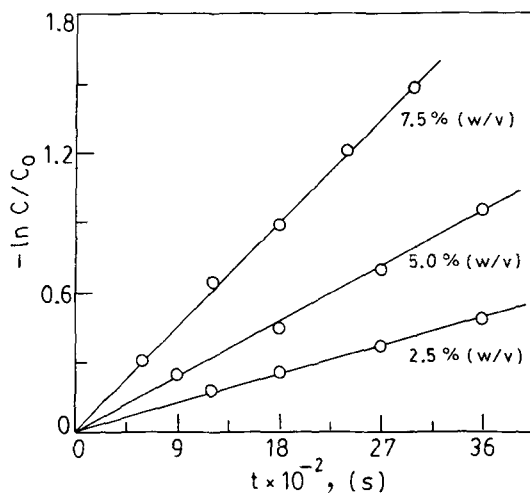
CONCLUSIONS

Our preliminary study shows that AM containing Si, Ti, Al, Fe, *etc.*-bearing phases can be an effective heterogeneous catalyst for aqueous phase decomposition of H_2O_2 under appropriate operating conditions. The catalytic effect of AM may be useful both in the treatment of hazardous effluents with H_2O_2 and also as an auto-catalyst in remediation of contaminated sites containing AM.
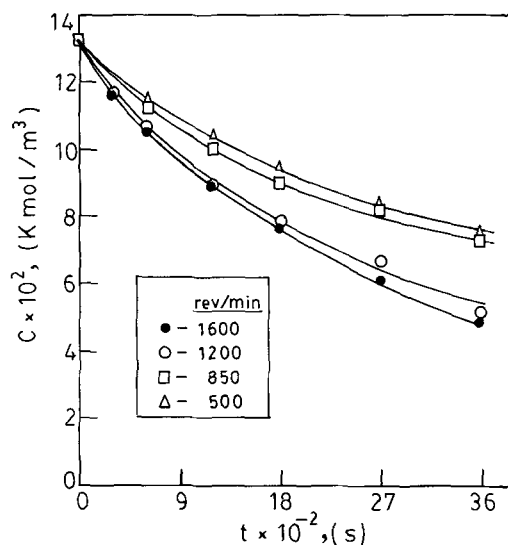

Figure 8.   Effect of speed of agitation on decomposition of H_2O_2 (Operating conditions: $V = 2.0 \times 10^{-4}$ m^3; $C_0 = 13.75 \times 10^{-2}$ kmol m^{-3}; $T = 313$ K; $W = 5\%$ (w/v); pH $= 9.24$).

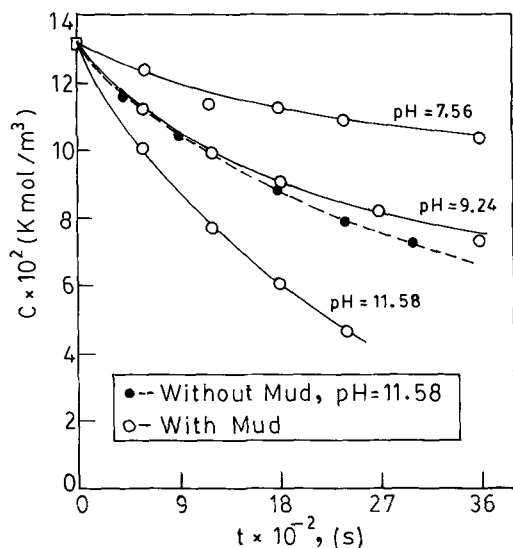Figure 9. Effect of pH on decomposition of H_2O_2 with and without alum mud (Operating conditions: $V = 2.0 \times 10^{-4}$ m³; $C_0 = 13.75 \times 10^{-2}$ kmol m⁻³; $T = 313$ K; $W = 5\%$ (w/v); $N = 850$ rev min⁻¹).

ACKNOWLEDGMENTS

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