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Amine screening for oxidation by bench-scale experiments

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Abstract

Amine oxidation is a major problem associated with CO_2 absorption using amine scrubbing. The oxidation of various amines has previously been studied, but the detailed mechanism of oxidation and the conditions under which amines are oxidized are still unclear. In general, primary amines are the most easily oxidized, followed by secondary and tertiary amines. In previous research, a study focused on the effect of the molecular structure of the amines has been reported[1]. In this work, oxidation experiments using the HGF (High Gas Flow reactor) and the ODBR (Oxygen Depletion Batch Reactor) were performed to understand the impacts of ferric iron, a known catalyst of amine oxidation, and to screen resistance to oxidation of several amines. The resistance was evaluated based on the generation rate of NH_3 in the HGF and the consumption rate of DO (dissolved oxygen) in the ODBR. The results show that piperazine (PZ) and 2-methylpiperazine (2-MPZ) were the most resistant to oxidation, and primary amines produced more NH_3. The DO rate and NH_3 generation were not equivalent, and the ratio of those two measurements was different for each amine.

Figure 1 shows the configurations of HGF and ODBR. In the HGF, air and CO_2 were supplied at desired rates using mass flow controllers (MFCs) and then introduced into the bottom of the reactor. The concentration of NH_3, amines, CO_2, and other degradation products in the gas phase is monitored by Fourier-transform infrared spectrometer (FTIR). The exhaust of the FTIR is recycled to the reactor and mixed with the inlet flow to provide good gas/liquid contact in the reactor and to amplify the accumulation of degradation products. In the ODBR, 500 mL/min of air is bubbled into the solution by the micro size gas dispersion tube for 5 minutes. The temperature of each experiment was controlled using a heated circulating water bath.

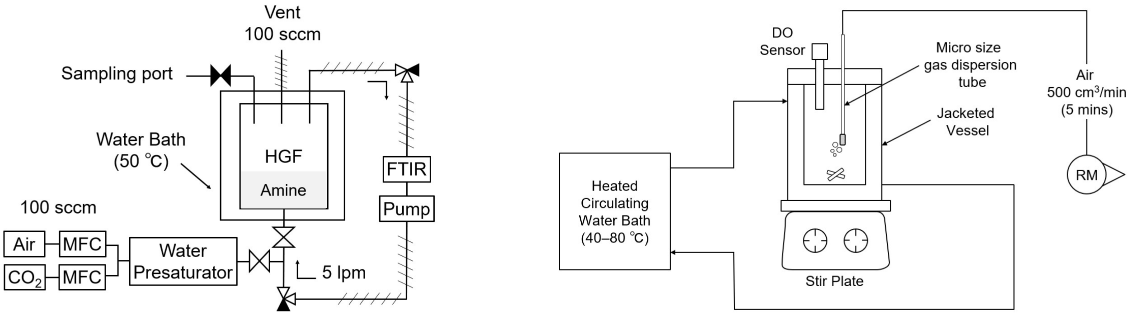

Figure 1: The configurations of HGF (left) and ODBR (right)

The concentration of all amines was prepared as 30 wt %, and the water bath temperature was set to 50 °C for HGF and 60 °C for ODBR. The CO_2 loading for HGF was set to achieve the equivalent loading at 50 °C with 2% CO_2 under atmospheric pressure. The equivalent loading of each amine was estimated from experimental data[2]. For the ODBR, CO_2 was loaded to achieve rich loading for each amine. Figure 2 shows NH_3 generation rate from MIPA (monoisopropanolamine) in HGF, and Figure 3 shows the DO consumption by MIPA in ODBR. The generation rate of NH_3 indicates that MIPA is oxidized just by oxygen contained in air. In both experiments, significant changes were observed when iron ions were added to the amine, and the NH_3 generation rate and DO consumption rate increased. When EDDA (ethylendiaminediacetic acid), which is known to complex with iron ions, was added to the amine, the NH_3 generation rate decreased rapidly. This suggests that the complex of EDDA with iron ions reduced the catalytic effect of iron ions and inhibited oxidation.

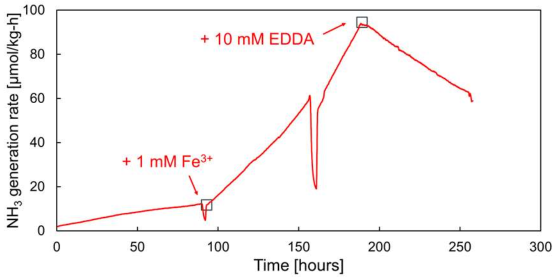

Figure 2: NH_3 generation rate in MIPA (HGF)

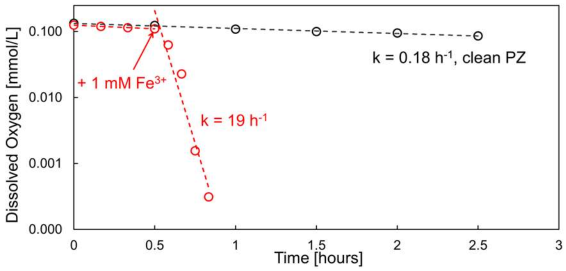

Figure 3: DO consumption in MIPA (ODBR)

Similar experiments were performed with various amines. The NH_3 generation rate and the rate constant for DO consumption are summarized in Table 1. The k_{50} for NH_3 generation was calculated based on the assumption that the stoichiometry of DO consumption is 1 mol DO/mol NH_3. When the rate constants of NH_3 generation and DO consumption are arranged in order of magnitude, the tendency seems to be generally the same. However, the rate constants of DO consumption are larger than those of NH_3 generation, and those of AMP, CESAR1, HEP, and MEA are 2 to 5 times larger. This suggests that when 1 mole of DO is consumed, not all the DO is consumed for the oxidation of degradation products that degrade to NH_3. It is possible oxygen is consumed in the oxidation of other degradation products that do not have a nitrogen atom in the molecule, like aldehydes. This suggests that NH_3 is not a degradation product directly generated when amines are oxidized, but that there are also intermediates. Another possibility is that the oxidation rate in the HGF takes longer to reach steady state than ODBR. Then the increase in NH_3 production rate means that steady state has not been reached, and therefore the rate constant results in smaller numbers. In some amines, such as AEP, the rate constants differ by more than 100 times, suggesting that comparing the rate constants of these two experiments may not be effective for screening amines. In the HGF experiments with MPA, 1-MPZ, and HEP, the initial NH_3 generation

Table 1: Summary of screening amines

Compound	Abbreviation	NH_3 generation		k of DO consumption [h^{-1}]	
		k_{50} [h^{-1}]	Rate range [μmol/kg-hr]	Baseline	+ 1 mM Fe^{3+}
Piperazine	PZ	0.009	0 - 4	0.14	0.78
2-methylpiperazine	2-MPZ	0.014	0 - 3.5	0.09	10.8
Aminomethylpropanol	AMP	0.032	2 - 5	0.18	2.1
1-methylpiperazine	1-MPZ	0.046	11 - 3		
2.5 m PZ/ 5 m AMP	CESAR1	0.050	0 - 70	0.12	17.4
Monoisopropanolamine	MIPA	0.058	0 - 95	0.26	19
Aminoethylpiperazine	AEP	0.092	0 - 45	24.6	34.5
Hydroxyethylpiperazine	HEP	0.092	4.5 - 3	0.28	2.77
Monopropanolamine	MPA	0.116	32 - 12		
Monoethanolamine	MEA	0.733	0 - 500	2.16	40.4
Diethylenetriamine	DETA	0.869	0 - 800	30.1	65.6
Methyldiethanolamine	MDEA			0.07	3.05

rate was high and then gradually decreased over time. For most amines, the NH_3 generation rate gradually increased and became relatively constant before adding iron ions as shown in Figure 2 for MIPA. It is possible some amines included impurities that were more easily oxidized than the principal amine and do not generate NH_3 when oxidized. The understanding of the decrease can be improved by considering the results of liquid phase analysis and by testing whether the decrease of NH_3 generation rate reaches zero or levels off at a certain rate and then increases by extending the experimental period.

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Keywords: amines; oxidation; ammonium; dissolved oxygen