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An insight into Ru/TiO_2 catalyzed wet air oxidation of N-ethylethanolamine in an aqueous solution

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ABSTRACT

The catalytic wet air oxidation of N-ethylethanolamine (EEA) over 5% (w/w) Ru/TiO_2 catalyst was investigated at 500 mg L^{-1} EEA concentration, in the temperature range of 423–473 K, O_2 partial pressure of 0.34–1.38 MPa and catalyst loading of 0.33–1.32 kg m^{-3} in a kinetically controlled regime. The fate of 'N' atom of EEA was also investigated. 5% Ru/TiO_2 was found to be effective catalyst for complete degradation of EEA and active in the conversion of –NH– group of EEA to N_2. The highest conversion of –NH– to N_2 was about 70% at 448 K. Under partial resistance to mass transfer the selectivity to N_2 was marginally enhanced. Ethylamine (EA) was formed as an intermediate and found to be relatively refractory. The kinetic data was modeled using the power law rate expression in terms of total organic carbon (TOC). The experimental data could be best correlated by Langmuir–Hinshelwood type reaction model involving dual site dissociative adsorption of O_2.

1. Introduction

N-Ethylethanolamine (EEA) is a member of the group of N-substituted aminoethanols, which appears in the aqueous effluent streams originating from manufacturing and its application industry. EEA is widely used in emulsifiers, dispersants, detergents, lubricants and chemical intermediates. Mimura et al. [1] and Vaidya and Kenig [2] have presented its use in CO_2 absorption. EEA is manufactured from renewable source (ethanol) and has a potential to replace existing alkanolamines in acid gas processing industry such as natural gas sweetening, ammonia plant and synthesis gas from coal or biomass gasification. It is well known fact that the alkanolamines used in gas processing industry undergo degradation due to some irreversible reactions with CO_2 over a period. This necessitates a proper effluent treatment process. It was, therefore, desired to have an efficient end of pipeline effluent treatment process that would help in conservation of water. The wet air oxidation (WAO) process [3–8] provides a viable advantage not only to treat such a waste stream containing amino compounds [9] but also to possible recycle of precious water.

All over the world environmental engineers would like to have total conversion of 'N' in any organic waste to N_2 not to NH_3 and its further oxidation to NO_x resulting in the formation of $NO_3{}^-$ and $NO_2{}^-$ ions in an aqueous solution. The specifications of $NH_4{}^+$, $NO_3{}^-$ and $NO_2{}^-$ ions in the aqueous stream are likely to become more and more stringent in years to come. While selective catalytic wet air oxidation of ammonia in aqueous solution to N_2 over supported catalysts consisting noble metals (Pt, Rd, Rh, Ru) and other catalytic elements (Co, Ni, Cr, Fe, Mn, Mo, Cu) is well understood [10–13], there is a considerable scope for systematic study of wet air oxidation of 'N' bearing organics. Recently, Reddy and Mahajani [14] have studied the fate of 'N' atom in heterogeneously catalyzed (Ru/SiO_2) WAO of aniline. Gunale and Mahajani [15] have reported the application of homogeneous catalyst, copper sulfate ($CuSO_4$), for the mineralization aqueous aniline. Therefore, it is important that, during wet air oxidation of 'N' bearing compounds, the N_2 selectivity should be highest. The catalytic wet air oxidation can provide possible answer to this by making operating conditions less severe. There is scanty information available in the published literature on the fate of 'N' atom originating from organic aliphatic amines present in various waste streams.

In the present paper, attention has been focused on conversion of secondary amino group (R_1–NH–R_2, where $R_1 = C_2H_5$ and $R_2 = C_2H_4OH$) to N_2, during catalytic WAO of EEA. Simultaneously, we also need to have efficient destruction of EEA and total organic carbon (TOC) of the system. Our experience with wet air oxidation of heterocyclic and aromatic amines indicates that, heterogeneous Ru catalyzed system is much more efficient in converting 'N' to N_2. It has also been reported that ruthenium (Ru) is not leached out by acetic acid, formed during the wet air oxidation [16,17]. We, therefore, present studies pertaining to destruction of EEA and associated TOC by Ru based heterogeneous catalyst. An attempt has been also made to maximize the selective conversion of 'N' in EEA to N_2.

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Nomenclature

A	oxygen
[A*]	concentration of oxygen in the bulk liquid phase (kmol m^{-3})
H_A	Henry's constant for oxygen (kg m^{-3} MPa^{-1})
K_A	adsorption equilibrium constant for A
K_{TOC}	adsorption equilibrium constant for TOC
k_t	reaction rate constant in Eq. (2) (($m^3)^{m+n}$ kg^{1-m-n} (kg cat.)$^{-1}$ min^{-1})
k_t'	reaction rate constant in Eq. (4) (($m^3)^n$ kg^{1-n} (kg cat.)$^{-1}$ min^{-1} MPa^m)
k_{st}	surface reaction rate constant of TOC reduction
m	order with respect to oxygen
n	order with respect to TOC
P_A	partial pressure of oxygen (MPa)
r_t	overall rate of reaction expressed in terms of TOC ((kg m^{-3}) (kg cat. $m^{-3})^{-1}$ min^{-1})
TOC	total organic carbon (kg m^{-3})
t	time (min)
η	effectiveness factor
ϕ	Thiele modulus
ΔH_{ad}	heat of adsorption (kJ mol^{-1})

2. Experimental

2.1. Chemicals

EEA was obtained from Merck Co. Ltd., Germany. Oxygen from a gas cylinder with a minimum stated purity of 99.5% was obtained from a local vendor. Ruthenium trichloride trihydrate ($RuCl_3 \cdot 3H_2O$) was obtained from SISCO Research Laboratories Pvt. Ltd., Mumbai. High surface area TiO_2 (Degussa P25, Germany) was used as a support. All the solutions were prepared in distilled water and for catalyst preparation deionized water was used. Ethylamine (EA) was obtained as gift sample from Alkyl Amines Chemicals Ltd., India. All analytical solutions were prepared in deionized water (unit Millipore, USA).

2.2. Catalyst preparation: formaldehyde reduction

The various supported Ru catalysts were prepared by the wet precipitation of ruthenium trichloride trihydrate on the support, described elsewhere [14]. The characterization of 5% Ru/TiO_2 was conducted by BET apparatus (Micromeritics Model ASAP 2010). The catalyst used exhibited BET surface area 64.62 m^2 g^{-1} and average pore diameter 343.44 Å. The particle size range was determined by using a particle size analyzer (Coulter LS 230). The mean particle diameter was 0.5 μm. A typical scanning electron micrograph (SEM) of the virgin catalyst is exhibited in Fig. 1, which shows that the catalyst particles are not spherical but highly irregular in shape. The loading of 5% (w/w) of Ru over TiO_2 was confirmed by the energy dispersive X-ray (EDX) analysis. The SEM and energy dispersive X-ray (EDX) analysis were performed on JEOL-JSM6380LA SEM instrument equipped with JED2300 series EDX system.

2.3. Experimental set up and procedure

The wet air oxidation studies were conducted in 1000 mL (SS 316) Parr High Pressure Reactor equipped with a Parr 4842 controller (Parr Instruments Company, Moline, IL, USA). The detailed descriptions of experimental set up and procedure are given elsewhere [14,15].

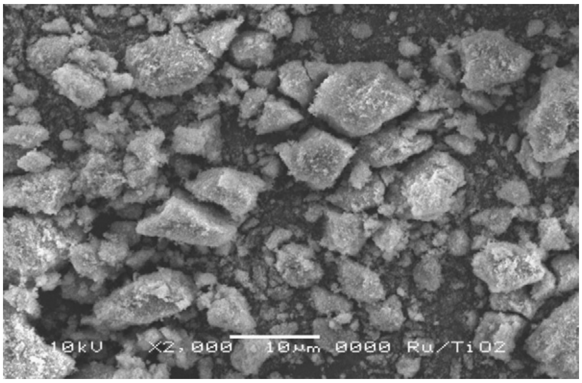


Fig. 1. Scanning electron micrograph of the 5% Ru/TiO_2 catalyst.

2.4. Analytical techniques

Total organic carbon (TOC) content of all samples collected during the course of the experiments was analyzed by "ANATOC SERIES II, TOC analyzer, SGE Australia". The high performance ion chromatograph (HPIC of DIONEX, Sunnyvale, CA, USA) using CS 14-A column with electro chemical detector (ED 50) in conductivity mode was used to analyze N-ethylethanolamine (EEA), ethylamine (EA) and NH_4^+ ions in aqueous solution. The eluent used was 10 mM methane sulfonic acid at 0.2 mL min^{-1} at 298 K. The contents of the liquid in the reactor vent gas absorber were also analyzed for $(NH_4)_2SO_4$ (basically for NH_4^+ ions) by HPIC.

The nitrate (NO_3^-) and nitrite (NO_2^-) ions were also analyzed on the same unit using Dionex AS 11 column. The eluent used was 12 mM NaOH at 0.1 mL min^{-1}. All eluents used for HPIC unit were prepared in deionized water.

The selectivity towards nitrogen gas (N_2) was computed via material balance across 'N' atom. The error in all experimental and analytical measurements never exceeded ±3%.

3. Results and discussion

Ru supported catalyst turned out to be obvious choice for heterogeneously catalyzed WAO studies as selective conversion of 'N' from EEA into N_2 gas. The various transport processes taking place in such systems have been comprehensively reviewed by Doraiswamy and Sharma [18]. The reaction could be mass transfer (diffusion) controlled (gas–liquid or liquid–solid transport) or kinetically controlled or both resistances might be significantly present. To discern the true chemical kinetics, it is absolutely necessary to eliminate inter and intraparticle diffusional resistances, i.e. to ensure the reaction is in true kinetically controlled regime with effectiveness factor almost unity.

3.1. Mass transfer considerations

The diffusional resistance for transfer of the dissolved oxygen from the gas-liquid interface to the bulk liquid phase (k_{La}) and then to the catalyst surface (k_{SLap}) can be ascertained by changing the intensity of turbulence in the liquid phase. In a slurry reactor where the catalyst is kept in suspension, the intensity of turbulence can be varied by changing the speed of agitation. Therefore, the effect of speed of agitation on the rate of TOC reduction was studied in the range of 600–1000 rpm at 473 K, 1.38 MPa oxygen partial pressure and catalyst (5% Ru/TiO_2) loading of 1.32 kg m^{-3}. The initial rates of TOC reduction varied from 0.008 to 0.009 (kg m^{-3}) (kg cat. $m^{-3})^{-1}$ min^{-1} as the speed of agitation increased from 600 to 1000 rpm. It was observed that the rate of TOC reduction was independent of the speed of agitation above

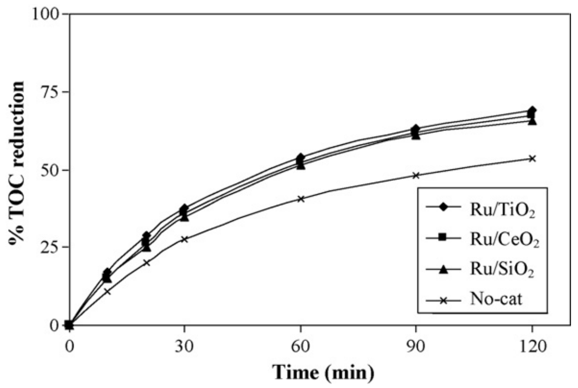


Fig. 2. Effect of heterogeneous catalysts on TOC reduction (448 K, O_2 partial pressure 0.69 MPa, catalyst loading 0.66 kg m^{-3}, initial EEA 500 mg L^{-1}).

an impeller speed of 800 rpm, thereby indicating the absence of mass transfer resistance to the transfer of oxygen in the bulk liquid phase and from the bulk liquid to the solid surface. So all further experiments were carried out at 1000 rpm.

To ascertain the presence of intra particle pore diffusion resistance Weisz–Prater criterion [19] was applied. The parameter $\eta\phi^2$ was calculated and found that it was far less than unity for both reactants. Hence the pore diffusional resistance was estimated to be absent. The mean particle diameter of the catalyst was around 0.5 μm. For such small particles, generally, the diffusional resistance offered by pores is absent. Thus it is seen that under the experimental conditions, all diffusional resistances were eliminated and a true kinetically controlled reaction regime was established for the kinetic interpretation.

3.2. Catalyst screening

Various supported Ru catalysts were selected for preliminary experiments. The catalysts were screened based on two criteria namely, the highest selectivity of –NH– group in EEA to N_2 and the ease of complete conversion of EEA. All experiments were conducted with 5%(w/w) Ru supported on TiO_2, SiO_2 and CeO_2 at temperature 448 K, 0.66 kg m^{-3} catalyst loading, 0.69 MPa of O_2 partial pressure, 1000 rpm speed of agitation and initial EEA concentration of 500 mg L^{-1} (TOC = 0.269 kg m^{-3}). Under these conditions there was no mass transfer resistance present in this gas–liquid–solid system. It was observed that in case of all these catalysts the complete destruction of EEA was observed within 10 min of the reaction. Fig. 2 depicts the catalyst performance in reducing TOC. It is seen that the heterogeneous catalyst has reduced the severe operating conditions by enhancing the TOC reduction. No ammonia was detected in the gas phase with these heterogeneous catalysts at the end of experiments. The formation of NH_4^+, NO_3^- and N_2 at the end of 120 min of reaction time is shown in Fig. 3. It is seen that 5% Ru/TiO_2 was a very good catalyst in the selective conversion of 'N' in EEA into N_2 gas. These observations also exhibited an interaction between the catalyst element and the solid support. It is interesting to note that for all catalysts studied there was no formation of NO_2^-, while NH_4^+ and NO_3^- ions were detected. The detailed studies of metal–support interaction have been excluded from the scope of the present investigation. There is a definite advantage of having this catalyst as in the absence of Ru catalyst, the selectivity towards N_2 was far less (almost 30%). Therefore 5% Ru/TiO_2 was selected as the catalyst for the WAO of EEA in the aqueous solution. Ru has been reported to be good catalyst for mineralization of acetic acid [16,17]. There was "ethylamine (EA)" formation in the presence of all the catalysts but Ru/TiO_2 resulted in highest selectivity towards N_2 (70%).

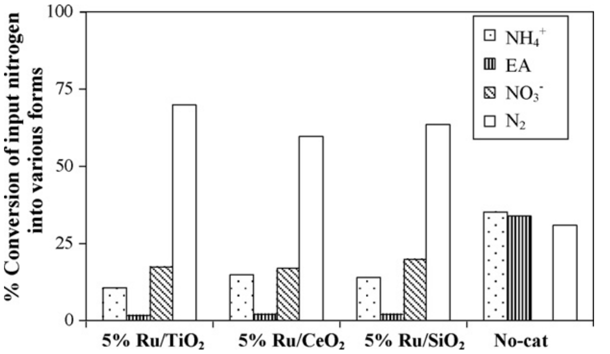


Fig. 3. Effect of heterogeneous catalysts on the formation of N_2 gas (448 K, O_2 partial pressure 0.69 MPa, catalyst loading 0.66 kg m^{-3}, initial EEA 500 mg L^{-1} (78.5 mg L^{-1} of nitrogen), reaction time 120 min).

3.3. Process parameter studies on the formation of N_2 gas

For the selective formation of N_2 gas, the various process parameters namely, temperature, catalyst loading and oxygen partial pressure were studied. The 'N' atom can get converted into NH_3 and N_2 gas. The low molecular weight acids formed during WAO process say acetic acid reacted in situ with NH_3 liberated forming ammonium acetate. This in turn gets oxidized to form NO_3^- and NO_2^-. Taguchi and Okuhara [12] and Lee [13] in their WAO studies of aqueous ammonia have reported that Ru/TiO_2 catalyst resulted in no N_2O formation. Therefore in the present investigation no attempt was made to analyze N_2O. We have considered that –NH– group is getting converted to N_2, NH_4^+, NO_3^- and NO_2^-. The residual TOC might reduce NO_3^- and NO_2^- to N_2. This sequence has been already postulated by Reddy and Mahajani [14]. There also exists a possibility of –NH– getting converted to NO_2^-/NO_3^- on the catalyst surface wherein NH_3 (NH_4^+ in aqueous solution) as an intermediate, gets oxidized by O_2 adsorbed on Ru catalyst site. When methyl or ethyl group is attached to 'N' atom as in the present case, there exists a distinct possibility of formation of methylamine (MA) or ethylamine (EA) as an intermediate, respectively.

3.3.1. Temperature

The operating temperature is expected to have considerable effect on the formation of N_2 gas. The experiments were conducted at 0.69 MPa oxygen partial pressure with the catalyst loading of 0.66 kg m^{-3} in the temperature range 423–473 K. The formation of NH_4^+, EA, NO_3^- and N_2 gas after 120 min of reaction at different temperatures is depicted in Fig. 4. At 423 K, though EEA was completely degraded, some EA was observed even after 120 min of reaction. However, at 473 K complete degradation of both EEA and EA was observed. The maximum selectivity towards N_2 formation was observed at 448 K (70%). However, at 473 K NO_3^- formation was the highest. The reduction in TOC takes place by two parallel paths namely, catalytic reduction in TOC by O_2 and also that by NO_3^- as postulated by Reddy and Mahajani [14]. At temperature above 473 K, the reaction with the adsorbed O_2 and N from EEA might be faster than that by NO_3^- oxidizing adsorbed organic substrate. Therefore, above this temperature, NO_3^- will remain in aqueous solution unless sufficient substrate is available for oxidation by NO_3^-. Degradation of –NH– group in the EEA at lower temperatures (below 448 K) resulted in more EA and NH_4^+ ion formation and at high temperatures (above 448 K) more NO_3^- ions were formed due to oxidation of NH_4^+ (NH_3 in water exists as NH_4^+ ions) to NO_3^-. Thus there is strong dependence of the selectivity towards N_2 on temperature. The highest selectivity to N_2 observed at 448 K was 70%.

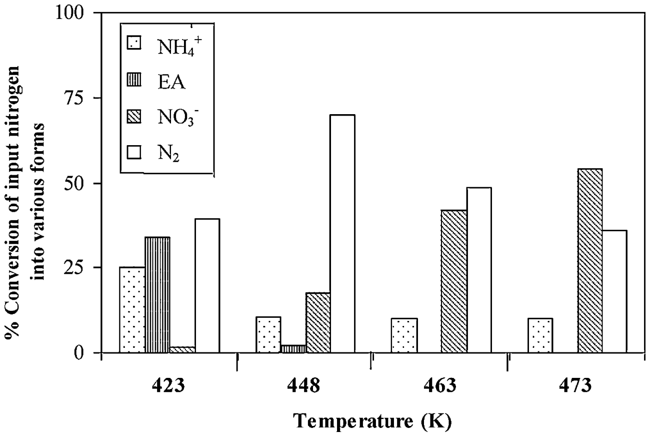


Fig. 4. Effect of temperature on the formation of N_2 gas (O_2 partial pressure 0.69 MPa, catalyst loading 0.66 kg m^{-3}, initial EEA 500 mg L^{-1} (78.5 mg L^{-1} of nitrogen), reaction time 120 min).

3.3.2. Catalyst loading

Experiments were performed at the catalyst loading of 0.33, 0.66, 0.99 and 1.32 kg m^{-3} at 448 K and at oxygen partial pressure of 0.69 MPa. As expected, the rate of TOC reduction and EEA degradation increased with the catalyst loading (Fig. 5). This is due to provision of more catalytic active centers for the reaction. Fig. 5 also exhibits the formation of NH_4^+, EA, NO_3^- and N_2 gas after 120 min of the reaction. It should be noted that no NO_2^- ions were detected. It was observed that at lower catalyst loading more EA and NH_4^+ ions were formed and at higher catalyst loading more NO_3^- ions were formed. So the catalyst loading 0.66 kg m^{-3} was found to be most favorable for maximum selectivity to N_2 (70%).

3.3.3. Oxygen partial pressure

The effect of O_2 partial pressure on the performance of catalyst was studied over the range of O_2 partial pressures 0.34–1.38 MPa at 448 K using a catalyst loading of 0.66 kg m^{-3}. The rates of reaction increased with an increase in O_2 partial pressure (Fig. 6). The formation of NH_4^+, EA, NO_3^- and N_2 gas after 120 min of reaction (Fig. 6) indicates that the selectivity towards N_2 formation increased up to O_2 partial pressure of 0.69 MPa and then decreased due to formation of NO_3^-. It is obvious that more O_2 would oxidize NH_3 to NO_3 resulting in formation of HNO_3 (NO_3^-). It is thus seen that on the catalyst surface various reactions take place simultaneously.

3.4. The influence of mass transfer resistance

In the industrial practice, WAO reaction is always influenced initially by mass transfer resistance (O_2 transfer in water) due to very high TOC (hence COD) exhibited by the actual waste. It is expected that mass transfer resistance should have a remarkable effect on the distribution of products of the reaction. Vaidya and Mahajani [20] have investigated the role of mass transfer limitations in the formation of acetic acid in non-catalytic WAO of phenol. So in the present study, to have better insight towards the formation of N_2, it was thought desirable to study the WAO in partly mass transfer controlled regime. For this purpose a comparison was done by carrying out the experiments at 473 K, 0.69 MPa oxygen partial pressure and 13.2 kg m^{-3} of catalyst loading in mass transfer controlled regime (at 200 rpm speed of agitation) and in kinetically controlled regime (at 1000 rpm) at initial EEA concentration of 10,000 mg L^{-1}. In both the regimes complete destruction of EEA was observed. Fig. 7 depicts the formation of NH_4^+, NO_3^- and N_2 gas after 120 min of reaction. It can be seen that in mass transfer controlled regime the selectivity towards the formation of N_2 is higher due to presence of finite excess TOC, which results in possible reduction of NO_3^- to N_2. Thus for mass transfer controlled regime is beneficial for the formation of more N_2 gas. This is an interesting observation. The commercial reactor would be a packed bubble column (the catalyst bed) or the monolithic catalytic reactor operated under mass transfer influence. A pilot plant hopefully will result in ascertaining product distribution. The present study and that by Vaidya and Mahajani [20] strengthen this belief.

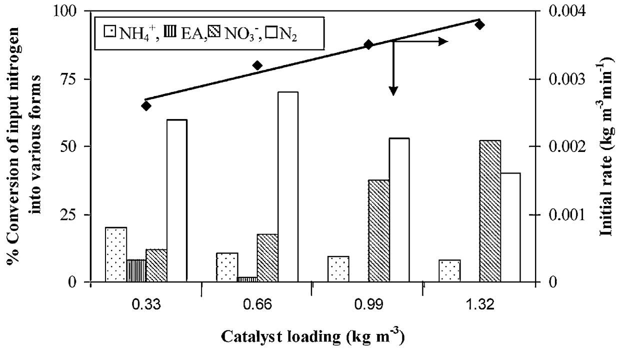


Fig. 5. Effect of catalyst loading on the initial rates of TOC reduction and formation of N_2 gas (448 K, O_2 partial pressure 0.69 MPa, initial EEA 500 mg L^{-1} (78.5 mg L^{-1} of nitrogen), reaction time 120 min).

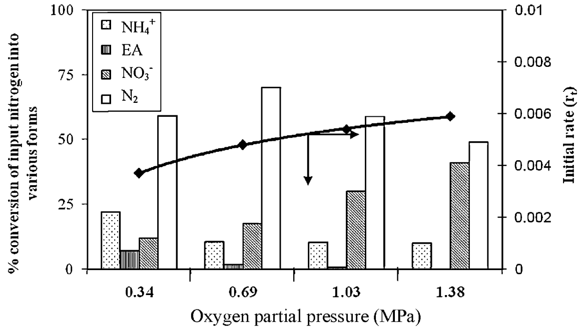


Fig. 6. Effect of O_2 partial pressure on initial rates of TOC reduction formation of N_2 gas (448 K, catalyst loading 0.66 kg m^{-3}, initial EEA 500 mg L^{-1} (78.5 mg L^{-1} of nitrogen), reaction time 120 min).

3.5. Reaction kinetics

The wet air oxidation of EEA as seen previously is a complex mechanism that proceeds through the formation of various intermediates (EA, acetic acid) through numerous pathways. An attempt was made to develop a kinetic rate expression for heterogeneous

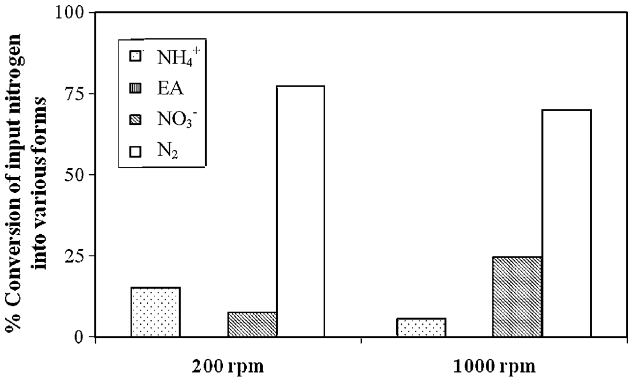


Fig. 7. Effect of speed of agitation on the formation of N_2 gas (473 K, O_2 partial pressure 0.69 MPa, catalyst loading 13.2 kg m^{-3}, initial EEA 10,000 mg L^{-1} (1570 mg L^{-1} of nitrogen), reaction time 120 min).

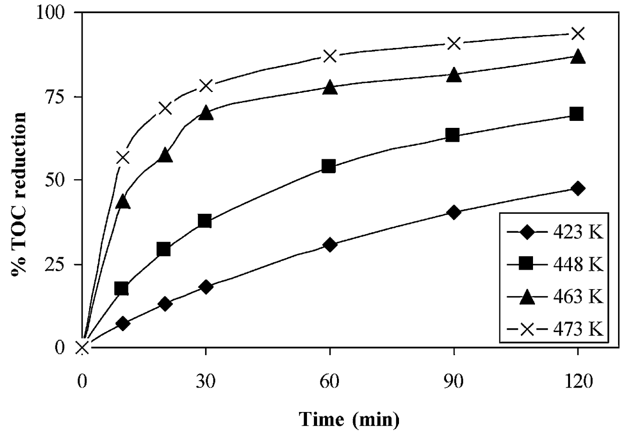
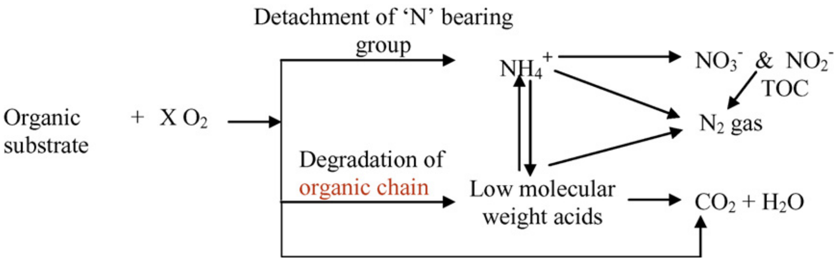


Fig. 8. Effect of temperature on the TOC reduction (O_2 partial pressure 0.69 MPa, catalyst loading 0.66 kg m^{-3}, initial EEA 500 mg L^{-1}).

catalytic wet air oxidation of EEA. The non-catalytic wet air oxidation of EEA is also possible under the conditions employed for this study as seen from Fig. 2. So, strictly speaking, the rates of reaction for non-catalytic wet air oxidation need to be subtracted from those observed in the presence of the catalyst in order to highlight the true effect of the catalyst on the rate of reaction. Due to the complex mechanism the modeling of each individual reaction would be a futile exercise. Therefore, a lumped parameter system in terms of TOC is proposed for kinetic data interpretation to aid process environment engineer.

In WAO, the reaction exhibits two different kinetic behaviors, namely the fast oxidation of organic substrate followed by mineralization of low molecular weight compounds formed such as acetic acid and oxalic acid. Being slower the second step becomes the rate-controlling step. In case of nitrogen bearing compounds the mechanism for degradation could be postulated as follows [14]:



(1)

The effect of temperature on TOC reduction was studied in the range of 423–473 K. The effect of temperature on TOC reduction is shown in Fig. 8. These TOC versus time profiles were analyzed by fitting into the polynomial expression and rates were deduced. Experiments were conducted at 448 K and 0.69 MPa oxygen partial pressure to study the dependence of the initial rates of reaction on the catalyst loading. As shown in Fig. 5, the initial rate varied linearly with the catalyst loading in the range 0.33–1.32 kg m^{-3}. The effect of oxygen partial pressure on TOC reduction was studied in the range of pressures 0.34–1.38 MPa at 448 K using a catalyst loading of 0.66 kg m^{-3}. The dependence of initial rate on the oxygen partial pressure is shown in Fig. 6. As the wet air oxidation progressed the pH of the solution changed from 11 (alkaline) to 3.5 (acidic) depending upon the operating conditions.

3.5.1. Model I: power law model

The simple process design engineer friendly model in any heterogeneous reaction is power law model, which represents macroscopic view. The active centers in any heterogeneous catalyst are directly proportional to the weight of the catalyst. Therefore the catalyst activity in terms of weight would be more process design engineer friendly entity rather than expressing results in terms of kinetic presentation expressed as turn over frequency (TOF).

Table 1
Rate constants and orders in power law model.

Temperature (K)	$k_t' \times 10^3$	m	n
423	10 ± 0.4	0.52 ± 0.04	0.98 ± 0.10
448	21 ± 0.5	0.60 ± 0.07	1.03 ± 0.14
463	59 ± 1.9	0.65 ± 0.10	1.11 ± 0.18
473	122 ± 3.1	0.71 ± 0.15	1.14 ± 0.21

Thus the rate of reaction in terms of TOC reduction can be expressed as:

$$r_t = k_t[A^*]^m[\text{TOC}]^n \tag{2}$$

The oxygen concentration in the liquid phase [A*], which is saturated solubility at equilibrium, is correlated to the partial pressure P_A via the solubility parameter H_A.

$$[A^*] = H_AP_A \tag{3}$$

Eq. (3) therefore can also be written as,

$$r_t = k_t[H_AP_A]^m[\text{TOC}]^n = k_t'[P_A]^m[\text{TOC}]^n \tag{4}$$

where $k_t' = k_t[H_A]^m$. Eq. (4) is the process design engineer friendly form of the power law rate expression. Eq. (4) was used to fit the reaction kinetic data obtained from TOC versus time profiles. The orders of the reaction, m and n, with respect to oxygen and TOC were obtained using linear regression. The values of k_t', m and n at various temperatures are given in Table 1 along with 95% confidence limits. Thus, the reaction orders (m and n) vary with temperature. The fractional order variation for O_2 concentration and TOC with respect to temperature pointed towards a more complex behavior at the microscopic/molecular level. The microscopic view of the system is best represented by series of various adsorption, desorption and kinetic terms in the rate expression.

3.5.2. Model II: support redox model

The support, TiO_2 crystal lattice when excited might donate its oxygen as in the case of photocatalysis for reaction with adsorbed organic substrate and itself get re-oxidized by molecular oxygen from solution. Maugans and Akgerman [21] in their studies on wet air oxidation of phenol over a Pt/TiO_2 catalyst have explored such mechanism and proposed a modified redox mechanism, which is named as support redox model in the present investigation, where a reaction between adsorbed organic substrate and the oxygen of the catalyst was assumed to be rate controlling. It is well known that Ru itself is a very good catalyst for oxidation of amino group and intermediate acetic acid. Therefore, it was thought desirable to ascertain the applicability of the model based on the reaction between adsorbed organic substrate (characterized by lumped parameter TOC) and the oxygen from the support. By using this mechanism, the correlation for the rate of TOC reduction can be

Table 2
Parameters for Eley–Rideal model.

Temperature (K)	k_{st} ((m^3)^2 kg^{-1} (kg cat.)$^{-1}$ min^{-1})	$K_{TOC} \times 10^4$	RSS
423	8.80 ± 0.9	53.7 ± 0.9	1.9×10^{-5}
448	17.40 ± 4.3	14.0 ± 0.6	1.3×10^{-5}
463	93.70 ± 9.5	7.5 ± 0.4	6.4×10^{-5}
473	248.48 ± 12.5	4.9 ± 0.2	2.1×10^{-4}

derived as:

$$r_t = \frac{k_{st}K_{TOC}[TOC]}{(1 + K_A{}^{0.5}[H_A]^{0.5}[P_A]^{0.5} + K_{TOC}[TOC])^2} \tag{5}$$

where $[O_2] = [H_A][P_A]$. The analysis of the experimental data by Eq. (5) resulted in the negative values of K_A, which is not acceptable. This model indicates that the rate depends inversely on the partial pressure of oxygen. But, in the present investigation the rates are increasing with pressure and the order with respect to pressure in the power law expression was found to be positive (Table 1 and Fig. 6). So the support redox model was found to be unsuitable to explain the observed kinetic behavior of the WAO of EEA.

3.5.3. Model III: Eley–Rideal (E–R) model

In this model, the adsorption of reactants (organic substrates contributing to TOC) bearing organics was assumed to be fast and surface reaction between the reactants and molecular oxygen from bulk liquid phase was assumed to be rate controlling. Based on steady state hypothesis model equation was developed as:

$$r_t = \frac{k_{st}K_{TOC}[H_A][P_A][TOC]}{1 + K_{TOC}[TOC]} \tag{6}$$

where $[O_2] = [H_A][P_A]$. The statistical analysis of the experimental data by using Eq. (6) was carried out by using non-linear regression analysis. The minimum values of residual sum of squares (RSS) were used as criterion for model validation. The interpretation of experimental observations using Eq. (6) was found to be unsatisfactory due to higher RSS values (Table 2) compared to those from dissociative Langmuir–Hinshelwood (L–H) model (Table 4). Hence, the E–R model was ruled out.

3.5.4. Model IV: Langmuir–Hinshelwood (L–H) model

Organic oxidation reaction is frequently modeled by the Langmuir–Hinshelwood (L–H) kinetics where an irreversible surface reaction between the reactants (organic substrates contributing TOC and oxygen) was assumed to be rate controlling. The dual site L–H models were postulated for non-dissociative and dissociative adsorption of oxygen. The following rate expressions were derived.

$$r_t = \frac{k_{st}K_AK_{TOC}[H_A][P_A][TOC]}{(1 + K_A[H_A][P_A] + K_{TOC}[TOC])^2} \quad \text{(non-dissociative L–H model)} \tag{7}$$

$$r_t = \frac{k_{st}K_A^{0.5}K_{TOC}[H_A]^{0.5}[P_A]^{0.5}[TOC]}{(1 + K_A^{0.5}[H_A]^{0.5}[P_A]^{0.5} + K_{TOC}[TOC])^2} \quad \text{(dissociative L–H model)} \tag{8}$$

where $[O_2] = [H_A][P_A]$. The experimental data fitted well to the dual site dissociative adsorption of oxygen far better than that of non-dissociative adsorption of oxygen. The RSS values and various rate parameters for non-dissociative and dissociative models are shown in Tables 3 and 4, respectively. The power law model resulted in approximately 0.5 order with respect to oxygen thereby strengthening the inference of dissociative adsorption of oxygen. The parity plot (Fig. 9) of the correlation (Eq. (8)) shows good agreement between predicted and observed overall rates. From the temperature dependence of k_{st}, activation energy for the surface reaction was found to be 96 kJ mol^{-1}. The adsorption equilibrium constants K_A and K_{TOC} were correlated to temperature using the van't Hoff equation. The values of heats of adsorption of oxygen and organic substrates contributing to TOC are also shown in Table 4.

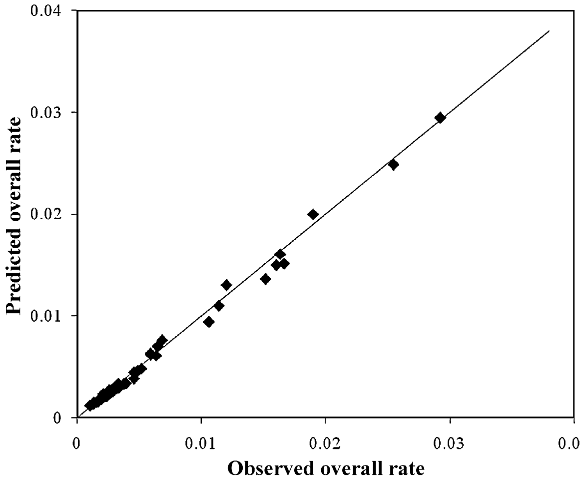


Fig. 9. Parity plot of dissociative L–H model.

Table 3
Parameters for the non-dissociative L–H model.

Temperature (K)	k_{st} ((m^3)^2 kg^{-1} (kg cat.)$^{-1}$ min^{-1})	$K_A \times 10^2$	$K_{TOC} \times 10^2$	RSS
423	0.65 ± 0.4	5.0 ± 0.6	5.4 ± 0.6	1.2×10^{-4}
448	9.22 ± 5.3	4.6 ± 0.5	5.1 ± 0.4	3.4×10^{-4}
463	45.90 ± 7.5	4.2 ± 0.3	4.9 ± 0.2	6.5×10^{-3}
473	126.40 ± 9.5	4.0 ± 0.1	4.8 ± 0.1	1.4×10^{-3}

Table 4
Parameters for the dissociative L–H model.

Temperature (K)	k_{st} ((m^3)$^{1.5}$ kg$^{-0.5}$ (kg cat.)$^{-1}$ min^{-1})	$K_A \times 10^4$	$K_{TOC} \times 10^3$	RSS
423	10.96 ± 0.2	72.1. ± 0.7	28.1 ± 0.5	8.5×10^{-7}
448	31.09 ± 1.3	55.01 ± 0.5	32.0 ± 0.3	2.1×10^{-6}
463	91.69 ± 5.5	44.8 ± 0.3	19.2 ± 0.2	3.3×10^{-6}
473	210.60 ± 15.5	43.7 ± 0.2	17.4 ± 0.1	5.6×10^{-6}
	ΔH_{ad} (kJ mol^{-1})	33.31	16.40	

3.6. Reusability of the catalyst

In order to study the reusability of this catalyst, four experiments were carried out on fresh solution of EEA with the same catalyst reused after separation by centrifugal separation. A marginal 3% loss in the activity of the catalyst was observed in terms of TOC reduction in 3 recycles. It should be noted that during wet air oxidation Ru is not leached out [16,17]. We also observed in our group the same for different systems. In reality, the activity study should be conducted with the actual waste samples coming out from a specific plant with the catalyst in the tablet or pellet or monolithic form to be used in the reactor.

4. Conclusions

The heterogeneous catalyst 5% Ru/TiO_2 was found to be very active in the complete degradation of EEA and in the conversion of -NH-group in EEA to N_2 gas. The highest selectivity towards N_2 gas formation was observed at the temperature of 448 K (70%). A dual site mechanism with dissociative adsorption of oxygen and surface reaction as the rate-controlling step provided the best fit of the experimental data.

The reaction under mass transfer controlled regime resulted in higher selectivity towards N_2 than that of kinetically controlled regime.

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