

## Catalytic incineration of organic vapors containing N, N-dimethylformamide

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### Abstract

N,N-dimethylformamide (DMF) vapor is a toxic air pollutant emitted mainly from the polyurethane synthetic leather manufacturing industries. In this work, the catalytic incineration of the dilute DMF vapor in air was investigated by using an externally heated, tubular fixed-bed reactor. A number of experiments were made to determine the global destruction efficiencies and the chemical kinetics for two commercial catalysts with Pt on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The reaction temperatures studied mediately ranged from 150°C to 300°C and the space velocities varied from 30000 to 60000 h<sup>-1</sup>. The results indicated that the reaction temperature was a determining factor in the catalytic incineration, and that the two catalysts under examination revealed no significant differences for the activity performance. The catalytic incineration of DMF with destruction efficiencies higher than 90% can be achieved at moderate incineration temperatures of 300°C or more, which were considerably lower than those of the direct thermal incineration. The experimental results were reasonably fitted by using the pseudo-first-order chemical reaction kinetics equations. A reaction scheme was also proposed and reasonably described the reaction kinetics of the catalytic oxidation of DMF.

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### 1. Introduction

In Taiwan, polyurethane (PU) is used mostly in the synthetic leather manufacturing [1], because it has some excellent properties, such as soft touching, high permeability, and tension-resistance. There are two kinds of manufacturing types in the production of the PU synthetic leather in which PU resin is dissolved by the solvents and then coated on the base clothes. The main difference is the application of various methods for extracting the solvents used in dissolving the PU resin. One is the dry-type process, which commonly employs solvents such as toluene, methyl ethyl ketone, ethyl acetate,

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Table 1  
Some common properties of DMF

Property	Value
Empirical formula	C <sub>3</sub> H <sub>7</sub> NO
Molecular weight	73.09 g/mol
Appearance	Colorless liquid
Boiling point	153 °C
Melting point	- 61 °C
Density (at 25 °C)	0.9445 g/cm <sup>3</sup>
Vapor pressure (at 20 °C)	0.32 kPa
Ignition temperature	455 °C
Flash point	58 °C
Flammable limit in air at 20 °C, 1 atm	
lower limit	2.2 vol%
upper limit	16.0 vol%
log <i>P</i> <sub>oct</sub> <sup>a</sup>	- 0.87- - 0.59 (calculated)

<sup>a</sup> *n*-octanol/water partition coefficient.

and N,N-dimethylformamide (DMF). The production is carried out by drying and vaporizing the solvents. Therefore, this dry-type process will emit the waste gas containing solvent vapors from the heating or drying process units. In the other one, the wet-type process, using DMF as the only solvent, the production is performed by washing with the DMF solution and then dried, also emitting DMF vapor. In addition to the application to the PU synthetic leather manufacturing, DMF is mainly used as a solvent for the manufacture of fibrous polyacrylonitrile. The emission of DMF vapor in these applications of DMF solvent thus causes a serious air pollution problem. The annual consumption of DMF in Taiwan has exceeded 30000 metric tons in 1991.

DMF is a colorless, high-boiling, highly polar hydrophilic, organic solvent with a weak characteristically amine-like odor. Table 1 lists some common properties of DMF [2]. This solvent, however, is toxic to the skin and liver after excessive exposure. Subjective complaints have included anorexia, gastric pain, nausea, vomiting, weight loss, headache, and neurasthenic and cardiac symptoms [3]. Accordingly, the occupational exposure limit is set at 10 ppm (30 mg/m<sup>3</sup>) in most countries [3]. Due to the toxicity of DMF, it has been listed as one of the hazardous air pollutants in title III of the US Clean Air Act Amendments of 1990 and its emission needs to be controlled.

DMF is a volatile organic compound (VOC), and the coating and drying units of the PU synthetic leather manufacturing plants are the main emission sources. It was reported that some plants may emit about 0.3 Nm<sup>3</sup>/s (at 70 °C) and 300-1200 ppm DMF in the vent gas [1]. Various technologies may be employed to control the emissions of VOCs discharged from the point sources. The most common approaches are the thermal and catalytic incineration, the carbon adsorption, the combined adsorption and incineration, the condensation and the absorption [4]. The choice is

often determined by the VOC concentration of the stream being controlled, because the control efficiency depends on the VOC concentration.

The catalytic incineration of VOCs has been widely used to control the gas emissions [5–8]. The principal advantages of the catalytic incineration processes include nearly complete destruction of organic contaminants in excess of 90%, and low operation cost savings. The catalytic incineration process offers not only the less energy usage due to its lower operating temperature, but also considerably the lower residence/space time, requiring less construction cost than the direct thermal incineration.

Studies on the catalytic incineration of organic vapors containing DMF have not been reported. The purpose of this paper was thus to evaluate the performances of two commercial catalysts for the destruction of toxic DMF in the bench-scale tubular fixed-bed reactor. The relationships between the conversion and the major system parameters, including reaction temperatures and space velocities, were determined and compared regarding the abilities to destruct the DMF vapors of lean concentration. All these experimental results were modeled by using the appropriate kinetic equations.

## 2. Experimental

### 2.1. Materials

DMF (reagent grade) was obtained from Fisher Scientific Co. The two commercial catalysts, mainly consisting of 0.5–1.5 wt% Pt supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, were employed in this study because these catalysts are available and widely used to control the emissions of industrial organic vapors in Taiwan. The Dash-220 catalyst, containing trace precious metal of Cr, was obtained from Engelhard Co. (Japan), and C-803 catalyst, also containing trace precious metals of Cr and Fe, from Shakubai Co. (Japan). The trace components of the catalysts mentioned above were analyzed by X-ray photoelectron spectroscopy (XPS). The catalysts were ground and correctly sieved to 40/50 ASTM mesh No. (0.36 mm) to reduce the intra-particle pore diffusion resistance for the use of all experiments. Their principal physical properties are given in Table 2.

### 2.2. Apparatus and procedures

A flow diagram of the fixed-bed catalytic reactor system is shown in Fig. 1. The compressed air from an oil-free cylinder was dried by silica gel in a packed-tube. The dried air was divided into two streams and metered to the system using two rotameters with needle valves. One air stream was passed through the DMF vapor saturator controlled by the thermostatic water bath. The other was used to dilute the saturation vapor in order to pick up the desired inlet flow rates and concentrations by the mixer. Following the static mixer, the feed stream entered the catalytic reactor.

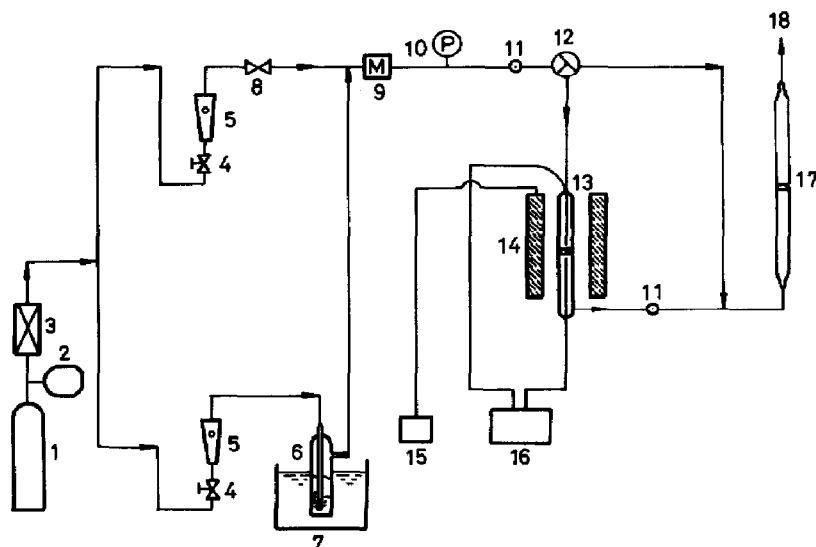
**Table 2**  
Physical properties of commercial catalysts (Pt on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) used in this study

Property	Catalyst	
	Dash-220	C-803
Apparent density <sup>a</sup> (g/cm <sup>3</sup> )	1.308	1.246
True density <sup>b</sup> (g/cm <sup>3</sup> )	3.245	3.332
Pore volume <sup>c</sup> (cm <sup>3</sup> /g)	0.45	0.47
Average pore diameter <sup>c</sup> (Å)	91	120
BET surface <sup>c</sup> (m <sup>2</sup> /g)	196	155

<sup>a</sup> Values were measured by mercury porosimeter (Micrometrics Inc., Model Autopore II 9200).

<sup>b</sup> Values were measured by helium-displacement pycnometer (Micrometrics Inc., Model AccuPyc 1330).

<sup>c</sup> Values were measured by area analyzer (Micrometrics Inc., Model ASAP 2000).



**Fig. 1.** Schematic flow diagram: (1) air cylinder, (2) regulation valve, (3) dryer, (4) needle valve, (5) rotameter, (6) DMF vapor generator, (7) thermostatic water bath, (8) nozzle, (9) mixer, (10) barometer, (11) sampling port, (12) three-way valve, (13) tubular catalytic reactor, (14) heating furnace, (15) temperature controller, (16) temperature recorder, (17) bubble meter, (18) vent.

The reactor with the catalyst bed in the middle section was housed in a compartment of 5 cm diameter by 40 cm length of electrical furnace to ensure uniform heating of the catalyst bed. The reactor temperature was controlled by the proportional integral derivative (PID) controller (Eurothem Co., Model 815P) to maintain a stable catalyst bed temperature to within  $\pm 1$  K of the set-point value. Following the reactor,

a portion of the effluent stream was sent to a gas chromatograph (GC) (Hewlett-Packard 5890 Series II) for analysis. The rest of the effluent stream was passed through an activated carbon adsorber and vented to a fume hood.

### 2.3. Catalytic reactor

The fixed-bed reactor consisted of a 1.5 cm OD 50 cm length Pyrex tube. The catalyst bed was supported on a porous Pyrex disc with glass wool, and located approximately 23 cm from the bottom of the reactor tube. The catalyst bed was prepared by mixing approximately 1.5 g of catalyst with crushed fine glass to minimize the axial mass and temperature gradients. Additional crushed glass and glass wool were also placed above the catalyst bed to serve as a preheating zone and gas distributor for the inlet feed gas.

### 2.4. Analytical methods

A manometer was used to measure the pressure drop of the packed catalyst bed. The temperatures of the gas stream entering and leaving the catalytic zone were measured by the chromel–alumel (K-type) thermocouples. The inlet and outlet concentrations were measured by a Hewlett-Packard 5890 Series II GC equipped with an 8 in. length, 1/8 in. OD stainless steel SP-100 column (Supelco, 60/80 Carboxpack), using a flame ionization detector (FID).

### 2.5. Experimental conditions

Only lean DMF vapor concentrations (say, 400 ppmv) were examined in order to practically simulate the actual conditions of exhaust gas in the field. Reaction studies were performed at mediate ranges (i.e. 150, 200, 230, 260 and 300 °C). Space velocities ( $V_s$ ), defined as the volumetric flow rate of feed divided by the catalyst volume, were varied in the range of 30000–60000 h<sup>-1</sup>. The effect of water on the incineration efficiency was not examined in the present work. To elucidate this effect, further study is called for. Process conditions were steadily maintained in order to assure the steady state within 5% relative error. Destruction efficiencies [ $X$ ,  $X = (C_0 - C)/C_0$ ] of DMF were determined from the concentrations of the feed ( $C_0$ ) and effluent ( $C$ ) streams measured by GC analysis. Generally, two to three runs were performed for each experimental case. The data presented here were the average values.

## 3. Results and discussions

### 3.1. Effects of temperature and space velocity on reaction performance

Figs. 2 and 3 present the conversion as a function of reaction temperature at space velocities of 30000, 36000, 45000, and 60000 h<sup>-1</sup> for catalysts Dash-220 and C-803, respectively. All these results were obtained at the same DMF inlet

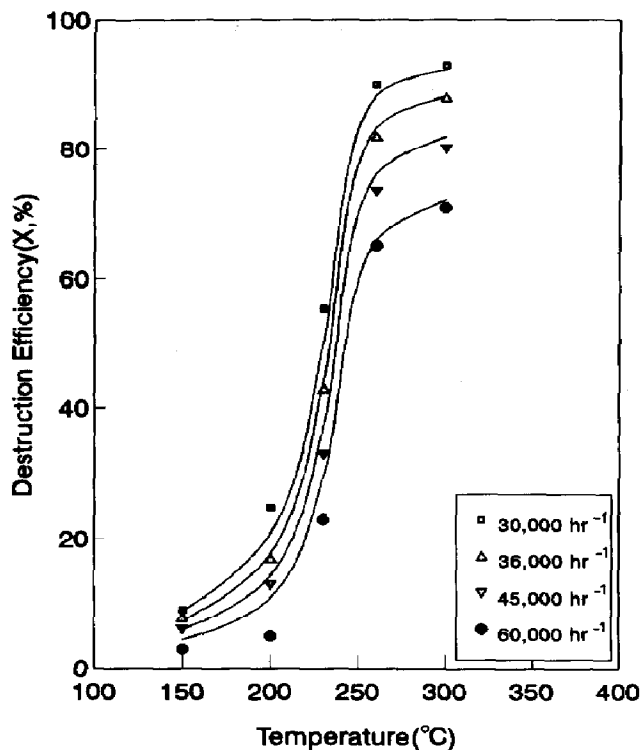


Fig. 2. Effect of  $T$  on  $X$  at  $C_0 = 400$  ppmv and various  $V_s$  for catalyst Dash-220.  $T$  = temperature ( $^{\circ}\text{C}$ );  $X$  = destruction efficiency (%);  $V_s$  = space velocity ( $\text{h}^{-1}$ ).

concentration of 400 ppmv. As expected, the DMF destruction efficiencies were found to be strongly influenced by the reaction temperature. The DMF can be destroyed with efficiencies greater than 90% when it was catalytically incinerated at 300  $^{\circ}\text{C}$  or more. The high performance efficiencies of catalytic oxidation of DMF were consistent with those of the other VOCs reported by previous investigators [5, 6, 8]. For example, the VOC destruction efficiencies reported by Jennings et al. [5] covers a range from 42.5% to 99%. These temperatures were significantly lower than those (about 750  $^{\circ}\text{C}$  or above) of direct thermal incineration. In addition, the DMF destruction efficiencies were influenced by the space velocity. A higher space velocity resulted in a lower destruction efficiency at the same temperature.

A comparison of performances between catalysts Dash-220 and C-803 may be made by examining the results of Figs. 2 and 3. No significant differences for the DMF destruction efficiencies between the two catalysts were observed. This is reasonable, if one notes that the two catalysts were both with Pt on  $\gamma\text{-Al}_2\text{O}_3$  and possessed about the same density, pore volume, average pore diameter, and BET surface area as given in Table 2. Furthermore, for both catalysts, some trace organic products other than DMF were detected by GC analysis. In general, the total concentration of these trace organics ( $C_{\text{org}}$ ) relative to that of DMF destroyed ( $= C_0 - C$ ) was lower than about 2%. This indicated that the selectivity of destruction of DMF into inorganics, which might possibly include  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{CO}$ , and  $\text{NH}_3$ , was generally higher

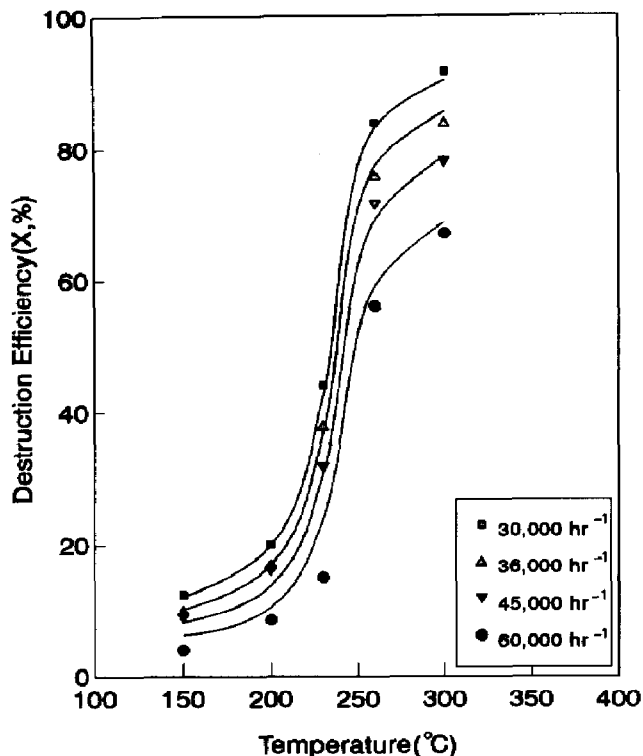


Fig. 3. Effect of  $T$  on  $X$  at  $C_0 = 400$  ppmv and various  $V_s$  for catalyst C-803.

than about 98%. Further works would be helpful in order to identify these organics other than DMF, and the inorganics.

### 3.2. Chemical reaction kinetics

In this study, an excess air was used as the dilution gas. Therefore, it is reasonable to assume that the oxidation would be pseudo-first-order reaction with respect to the solute, because the oxygen in air was also excessive [9, 10]. For the first-order kinetics with respect to the DMF, the reaction rate constant ( $k$ ) may be related to the fractional conversion ( $X$ ) of DMF as [11, 12]

$$\ln(1 - X) = -kt \quad (1)$$

The so-called space time,  $t$ , is defined as the reciprocal of the space velocity. A straight line plot of  $\ln(1 - X)$  vs.  $t$  would give the value of  $k$ .

Figs. 4 and 5 are the plots of  $\ln(1 - X)$  vs.  $t$  at various reaction temperatures for catalyst Dash-220 (with correlation coefficients,  $R^2$  of 0.86–0.99) and C-803 (with  $R^2$  of 0.94–0.99), respectively. Since the data presented here were average values,  $R^2$  was thus estimated according to these values. The results indicated a straight-line relationship between  $\ln(1 - X)$  and  $t$ , which thus supported that the assumption of first-order reaction is reasonable.

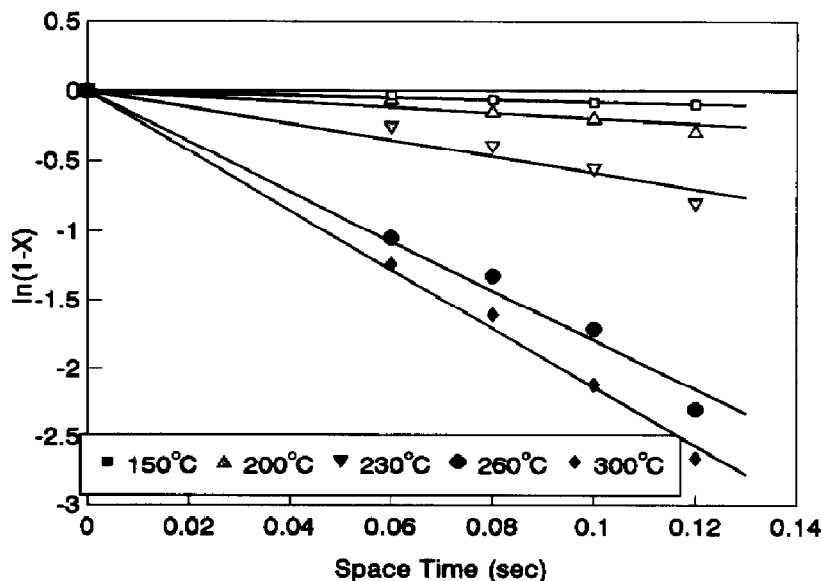


Fig. 4. Plots of  $\ln(1 - X)$  vs. space time at  $C_o = 400$  ppmv and various temperatures for catalyst Dash-220.

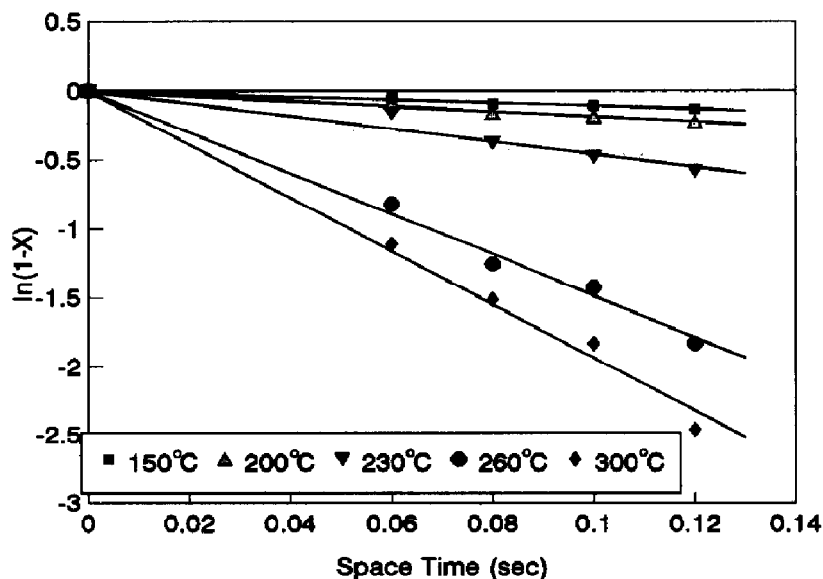


Fig. 5. Plots of  $\ln(1 - X)$  vs. space time at  $C_o = 400$  ppmv and various temperatures for catalyst C-803.

According to the Arrhenius equation, the reaction rate constant ( $k$ ) can be described as follows:

$$\ln k = \ln A - E/RT \quad (2)$$

where  $A$  is the pre-exponential factor,  $E$  is the activation energy,  $R$  is the ideal gas law constant, and  $T$  is the absolute temperature.



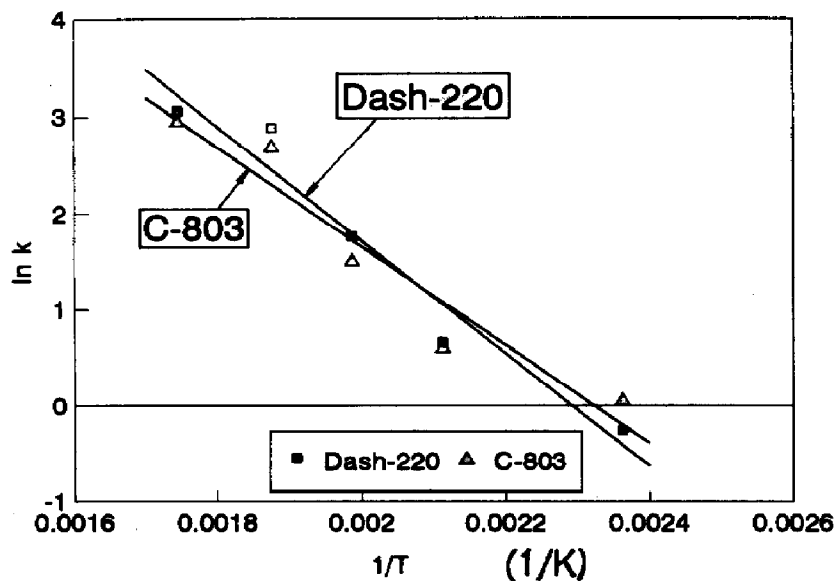


Fig. 6. Arrhenius plots of rate constants for catalysts Dash-220 and C-803.

Table 3

Best fit constants<sup>a</sup> for catalytic incineration of DMF based on Arrhenius rate equation

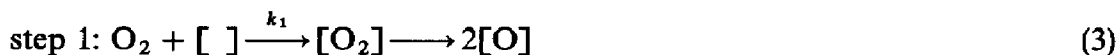
Kinetics constant	Catalyst	
	Dash-220	C-803
Pre-exponential factor $A$ (1/s)	716626	149883
Activation energy $E$ (kcal/mol)	11.7	0.2
$R^2$	0.95	0.92

<sup>a</sup> Constants are based on a linear least squares analysis of a global first-order model for catalytic decomposition in an isothermal tubular fixed-bed reactor.

Fig. 6 presents the Arrhenius plots for the catalytic incineration of DMF for the two catalysts, respectively. In all cases, reasonably good linear plots were obtained with correlation coefficients ( $R^2$ ) of 0.95 and 0.92 for catalyst Dash-220 and C-803, respectively. Table 3 summarizes the kinetic parameters obtained from the kinetic analysis. Using these kinetic parameters along with Eqs. (1) and (2), one may reconstruct the performance curves of  $X$  vs.  $T$  in Figs. 2 and 3 where space velocity is the reciprocal of space time. The activation energies of the two catalysts were about the same with values of 11.7 and 10.2 kcal/mol, respectively. These results were consistent in that both catalysts were with Pt on  $\gamma$ - $\text{Al}_2\text{O}_3$ . Also, the obtained activation energies for the oxidation of DMF were in the same order of magnitude as those of some  $\text{C}_3$

organic compounds over platinum catalysts. For example, the activation energies of Pt catalytic oxidation of  $C_3H_8$  and  $C_3H_6$  are 17 and 17.7 kcal/mol, respectively [13].

Regarding the above reasonable agreement of the results with the first-order reaction kinetics, one may postulate that the catalytic oxidation of DMF takes place with two steps. Namely,



Reaction (3) represents the adsorption of oxygen molecule on the surface active site (denoted as  $[ ]$ ) of catalyst. The adsorbed oxygen molecule is then decomposed as the active oxygen atom. This route is typical for the oxidation of common hydrocarbons employing noble metal catalysts [14, 15]. In reaction (4), the active oxygen atom reacts with the gaseous molecule of DMF and yields the products P. The reaction rates,  $r_1$  and  $r_2$ , of reactions (3) and (4), respectively, may be expressed as

$$-r_1 = k_1 C_{O_2} (1 - \theta) \quad (5)$$

$$-r_2 = k_2 C_{DMF} \theta \quad (6)$$

The other notations of expressions (3)–(6) are as follows:  $k_1$ ,  $k_2$  are the reaction rate constants of (3) and (4),  $C_{O_2}$ ,  $C_{DMF}$  are the concentrations of  $O_2$ , DMF and  $\theta$  is the fraction of catalyst surface occupied by  $O_2$ .

A pseudo-steady-state condition then leads to

$$k_1 C_{O_2} (1 - \theta) = \alpha k_2 C_{DMF} \theta \quad (7)$$

where  $\alpha$  is the number of oxygen molecules used in destructing DMF. Substitution of  $\theta$  obtained from Eq. (7) into Eq. (6) gives the reaction rate,  $r$ , as

$$-r = (k_2 C_{DMF}) / [1 + (\alpha k_2 C_{DMF} / k_1 C_{O_2})] \quad (8)$$

The rate expression of Eq. (8) illustrates the oxidation of DMF with Pt/ $\gamma$ - $Al_2O_3$  catalyst that follows an Eley–Rideal mechanism [16], which involves attraction of oxygen to Pt and reaction of DMF from the gas phase with the adsorbed oxygen. Noting the strong adsorption of noble metal with the oxygen molecule [14] and the excessive use of air in this study, one thus has  $C_{O_2} \gg C_{DMF}$  and  $(\alpha k_2 C_{DMF} / k_1 C_{O_2}) \ll 1$ . Then Eq. (8) becomes

$$-r = k_2 C_{DMF} \quad (9)$$

which is a first-order reaction with respect to DMF. This was consistent with Eq. (1). The reaction scheme proposed herein thus reasonably provided the theoretical basis for the chemical reaction kinetics analysis of this work.

#### 4. Conclusions

The toxic air pollutant of DMF vapor can be decomposed effectively by employing the technology of catalytic oxidation. The reaction temperature is a very important parameter in the catalytic incineration of DMF. High conversions (over 90%) may be achieved at the moderate reaction temperatures of 300 °C or more. The conversion of DMF increases as the space velocity decreases. The catalytic incineration of DMF can be reasonably fitted by the first-order chemical reaction kinetics equations. Also the reaction kinetics was reasonably described by the proposed reaction scheme.

#### 5. Acknowledgements

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