Oxidative decomposition of *N*,*N*′-dimethylformamide over Pt catalysts with H_2 addition to the feed

Junko Uchisawa*, Tetsuya Nanba, Shouichi Masukawa, and Akira Obuchi

Catalytic and Electrochemical Purification Group, Institute for Environmental Management Technology, National Institute of Advanced Industrial Science and Technology (AIST), 16–1 Onogawa, Tsukuba 305-8569, Japan

Received 4 July 2004; accepted 27 July 2004

Catalysis of decomposition of dilute *N*,*N*′-dimethylformamide was explored. Among the catalysts investigated, Pt displayed the highest activity at low temperatures (~200 °C) and DMF conversion was promoted by H_2 addition to the feed. As the Pt support material, H-ZSM-5 exhibited the best performance at around 200 °C in terms of harmless decomposition.

KEY WORDS: H_2 addition; H-ZSM-5; *N*,*N*′-dimethylformamide; oxidative decomposition; Pt catalyst.

1. Introduction

N,*N*′-dimethylformamide (DMF) is a volatile organic compound used in industrial applications, such as an amphiphilic solvent for organic syntheses and catalytic reactions, and as a gas adsorbent. It is mainly emitted from chemical factories in low concentrations but in high volumes of ventilated air. As it is designated as a hazardous material under the Clean Air Act Low in Japan, it is necessary to develop countermeasures to reduce dilute DMF in these exhausts. Catalytic oxidation is a desirable method in terms of energy savings because it generally proceeds at much lower temperatures and reactant concentrations than incineration. However, with oxidative decomposition, even using a catalyst, the nitrogen atoms contained in organic molecules tend to be converted to hazardous nitrogen oxides (NO and NO_2). A catalytic system must be sought that can convert the nitrogen in DMF to harmless N_2, while simultaneously obtaining CO_2 and H_2O as completely oxidized products. Very few reports have detailed catalytic oxidation of amines and amides. Okumura *et al.* [1] reported that binary catalysts of Au–Ir and Pt–Ir showed high activity for oxidative decomposition of $(CH_3)_3N$, but product selectivity was not mentioned. In the present work, we evaluated catalysts appropriate for DMF decomposition and also investigated the effect of H_2 addition to the feed on the activity. Although a typical reductant, H_2 is known to promote some catalytic oxidation processes, e.g., liquid phase oxidation of cyclohexane over Pt mixed with heteropoly compounds [2], and partial oxidation of benzene to phenol over Pt- and Pd–VOx/SiO_2 [3], Pd–Fe zeolite [4] and Pd membrane [5]. The addition of H_2 in these cases increased the object reaction rates while simultaneously suppressing over-oxidation. We expected a similar effect for H_2 addition in the catalytic oxidation of DMF and an increase in selectivity of conversion to N_2.

2. Experimental

The supported catalysts listed in Table 1 were prepared using the incipient-wetness method. Specifically, Al_2O_3 was impregnated with an aqueous solution of the starting materials of Pt, Pd, Rh, Cu and Mn, all of which are generally known as active oxidation catalysts, and was then calcined at 500 °C in air. Pt catalysts loaded over H-ZSM-5, SiO_2 and ZrO_2 were similarly prepared to investigate the effect of the support material. BET specific surface areas of the prepared samples were measured with a flow-type BET measurement apparatus (Nikkiso, Model 4232, Japan) and dispersions of the platinum-group metal (M) were estimated from the specific amount of CO adsorption: CO/M (mol/mol), by a pulsed CO chemisorption apparatus (Ohkura Riken, Model R6015H, Japan). The characterization results are also listed in Table 1.

Catalytic activity tests were carried out using a fixed-bed flow reactor. The catalysts (0.5 g), installed in a tubular quartz reactor (10 mm in inner diameter), were pretreated at 500 °C for 1 h under a flow of reactant gases (0.5 dm^3 (STP)/min) comprising 0.03% DMF, 0 or 1% H_2, 0 or 1% H_2O, and 10% O_2 balanced with He, and were then cooled by 2 °C/min. The concentrations of gaseous components were continually measured using a micro gas chromatograph (Varian, CP-2003, The Netherlands) for CO_2, CO, H_2, N_2 and N_2O, and an FT-IR spectrometer (Nicolet; Nexas 470, USA) equipped with a multi-reflectance gas cell (2 m in optical length) for NO, NO_2, NH_3, HCN, dimethylamine (DMA) and DMF. The catalytic activity was evaluated by DMF conversion to CO_2, and by H_2 conversion. The

---

*To whom correspondence should be addressed.
E-mail: junko-uchisawa@aist.go.jp

1011-372X/04/1100–0103/0 © 2004 Plenum Publishing Corporation

Table 1. Catalyst sample list

Active metal	Loading (wt%)	Starting material	Support composition/Manufacturer/Code	Surface area ($m^2\ g^{-1}$)	Metal dispersion (%)
Pt	1	H_2PtCl_6	Al_2O_3/Sumitomo Chemical/KHS-46	155	81
	1	H_2PtCl_6	H-ZSM-5/Tosoh/HSZ-820NAA origin	385	15
	1	H_2PtCl_6	SiO_2/Wako Chemical/Wakogel	439	36
	1	H_2PtCl_6	ZrO_2/Daiichi Kigenso/RST-H	36	60
Pd	1	$Pd(NO_3)_2$	Al_2O_3/Sumitomo Chemical/KHS-46	171	30
Rh	0.5	$Rh(NO_3)_3$	Al_2O_3/Sumitomo Chemical/KHS-46	180	57
Cu	5	$Cu(NO_3)_2$	Al_2O_3/Sumitomo Chemical/KHS-46	116	–
Mn	6	$Mn(CH_3CO_2)\cdot 4H_2O$	Al_2O_3/Sumitomo Chemical/KHS-46	171	–

temperature for which 50% DMF conversion to CO_2 occurred was designated T_{50}. The selectivities for conversion to the nitrogen-containing products were also estimated. The conversions and selectivities were defined as follows:

DMF conversion to $CO_2 = $(outlet CO_2 (ppm)/(inlet DMF (ppm)×3)×100 (%),

H_2 conversion = (outlet H_2/inlet $H_2 \times 100$(%).

Selectivity to nitrogen-containing products: $N_2 = (N_2 \times 2/\text{inlet DMF}) \times 100$ (%), $N_2O = (N_2O \times 2/\text{inlet DMF}) \times 100$ (%), $NO = NO/\text{inlet DMF} \times 100$ (%), $NO_2 = NO_2/\text{inlet DMF} \times 100$ (%), $NH_3 = NH_3/\text{inlet DMF} \times 100$ (%), $HCN = HCN/\text{inlet DMF} \times 100$ (%), $DMA = DMA/\text{inlet DMF} \times 100$ (%).

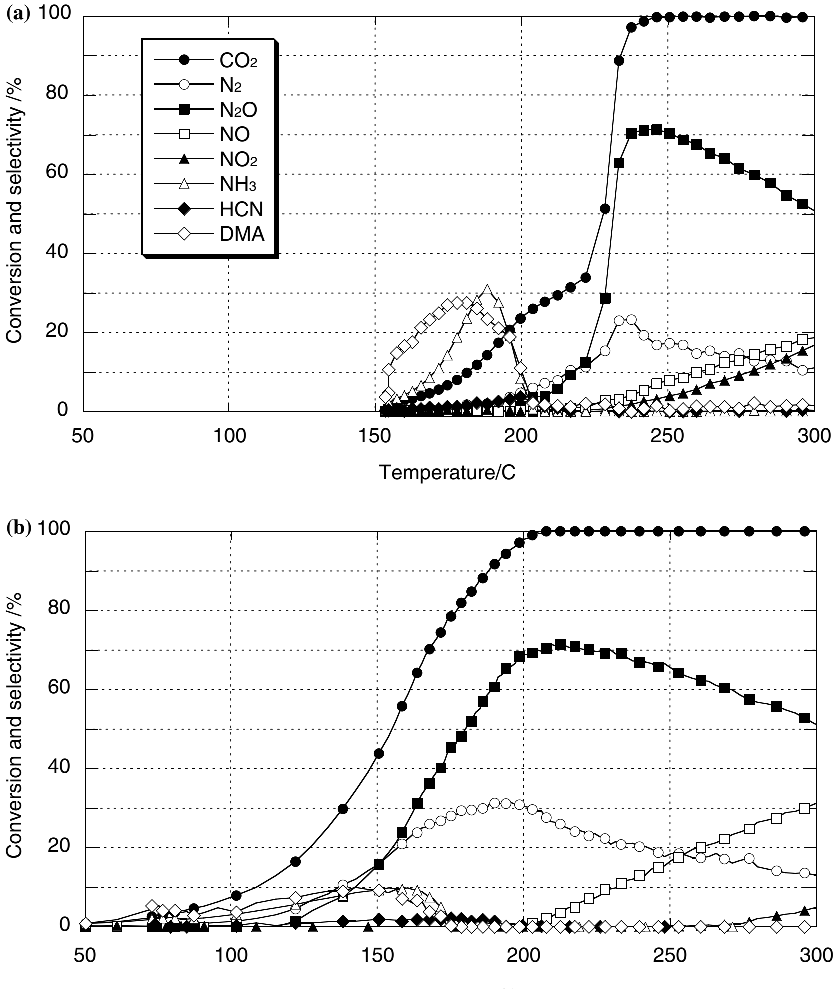

Figure 1. Effect of H_2 addition on the catalytic activity for *N,N′*-dimethylformamide (DMF) decomposition over $1\%PtAl_2O_3$. (a) $0.03\%DMF + 10\%O_2$; (b) $0.03\%DMF + 10\%O_2 + 1\%H_2$.

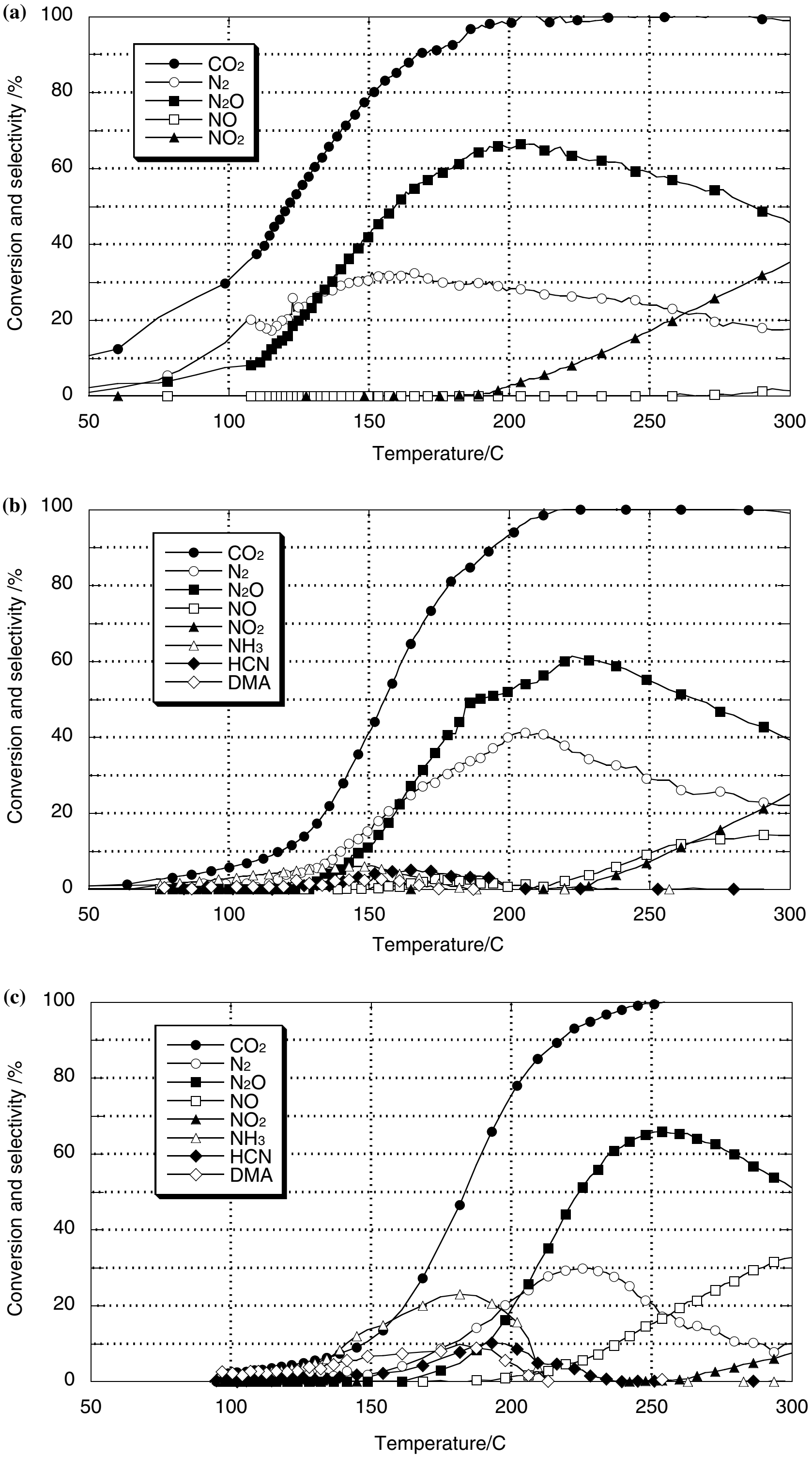

Figure 2. N,N'-dimethylformamide (DMF) decomposition over 1%Pt loaded on various support in the presence of 10%O_2 + 1%H_2. (a) H-ZSM-5; (b) SiO_2; (c) ZrO_2.

3. Results and discussions

3.1. Catalyst screening

Table 1 summarizes the catalytic activities of the metals supported on Al_2O_3 for DMF oxidative decomposition in the presence of 10% O_2, or 10% $O_2 + 1\%$ H_2. In the presence of only O_2, T_{50} values decreased in the order of Pt, Mn, Pd, Cu, and Rh. In the presence of $O_2 + H_2$, DMF conversion to CO_2 was evidently higher over the Pt and Pd catalysts than for O_2 alone, with the

Table 2
Catalytic activity for *N*,*N*′-dimethylformamide (DMF) decomposition

Catalyst	Without H_2	With H_2	
	T_{50}/°C	T_{50}/°C	H_2conv./% at T_{50}
1%Pt/Al_2O_3	230	155	86
1%Pd/Al_2O_3	232	183	100
0.5%Rh/Al_2O_3	280	290	89
5wt%Cu/Al_2O_3	228	224	2
6wt%Mn/Al_2O_3	224	225	1

T_{50} for Pt and Pd shifting to lower temperature by 75 and 49 °C, respectively.

Figure 1 shows the temperature trends of DMF oxidative decomposition over Pt/Al_2O_3 under the conditions shown in Table 1. In the presence of only O_2 (figure 1a), CO_2 production was initiated at 150 °C and reached 100% at around 250 °C. The production of N_2 and N_2O started at 150 °C, increasing and then decreasing after a maximum at around 240 °C. NH_3 and DMA were produced between 150 and 200 °C and their selectivity reached up to 30%. HCN was also produced below 200 °C, up to a maximum of 12 ppm. NO and NO_2 were produced above 220 °C and increased with temperature. In the presence of $O_2 + H_2$ on the other hand (figure 1b), production temperatures were shifted lower for all gases except for NO_2. CO_2 production started as low as 50 °C. Of note, the selectivity of conversion to NH_3 and DMA prominently decreased.

Pd/Al_2O_3 generated higher N_2 selectivities (60% at 275 °C) in DMF + O_2 + H_2, but also produced greater amounts of NH_3 and DMA than Pt/Al_2O_3, especially NH_3, for which selectivity reached as high as 70%.

The catalyst bed temperature was increased by 40~100 °C by 1% H_2 addition because of the heat released by $H_2 + O_2$ reaction. However, since the thermocouple for measuring the reaction temperature was placed in the center of the catalyst bed, the effect of this temperature rise is not the cause of the promoted DMF reaction. H_2O derived from H_2 might help promote DMF decomposition, and thus we performed DMF decomposition in the presence of 10% O_2 + 1% H_2O over Pt/Al_2O_3. DMF conversion occurred in almost identical activities and selectivities as in the presence of O_2 alone. Consequently, we concluded that the promotional effect was not due to H_2O.

The reported promotion of reactions using H_2 in the presence of O_2 over Pt or Pd catalysts has been suggested as resulting from formation of hydroperoxide species [2,4] or activated oxygen [5]. At present, the mechanism of promotion of DMF oxidative decomposition by H_2 addition is not clear, but it may be due to such intermediates. To clarify, it would be necessary to identify the active intermediates in the $H_2 + O_2$reaction over Pt and to investigate their reactivity with DMF and its byproducts.

3.2. *Effect of support material*

The effect of Pt support material on DMF oxidative decomposition in the presence of H_2 was investigated. Figure 2 shows the temperature dependency for Pt/H-ZSM-5, Pt/SiO_2 and Pt/ZrO_2. In the case of Pt/H-ZSM-5 (figure 2a), DMF was completely converted to CO_2 at 200 °C, while emissions of NH_3, HCN and DMA were negligible at all temperatures investigated. NO_2 was produced above 200 °C. In the case of Pt/SiO_2 on the other hand, a small amount of NH_3 (maximum selectivity 8%), HCN (5%) and DMA (2%) were produced below 200 °C. For Pt/ZrO_2, higher amounts of NH_3 (22%), HCN (10%) and DMA (10%) were produced below 230 °C. From these results and those for Pt/Al_2O_3(figure 1b), the order of activity of the support materials was found to be: H-ZSM-5 > $SiO_2 \sim Al_2O_3$ > ZrO_2. Incidentally, the T_{50} values for Pt/H-ZSM-5, Pt/SiO_2 and Pt/ZrO_2 in the presence of H_2 were decreased by 79, 22 and 41 °C, respectively, compared to each case without H_2.

We consider that the affinity between the support material and reactant/byproduct have a large effect on the reactivity of DMF oxidative decomposition. Basic DMF as well as the NH_3 or DMA produced from DMF tend to adsorb on acidic H-ZSM-5 and then further react until complete decomposition. H-ZSM-5 is also regarded to perform as a catalyst to selectively produce N_2 from NH_3 and NOx [6], both of which are intermediate products of DMF. In contrast, the reactants and byproducts hardly adsorbed on basic ZrO_2 [7,8], and thus would be easily released outside of the reaction system. SiO_2 displayed a medium activity between that of H-ZSM-5 and ZrO_2, probably due to not having either strong acidity or basicity [9].

In conclusion, Pt supported on H-ZSM-5 at around 200 °C under H_2 addition was the most desirable catalytic system tested in terms of harmless decomposition of DMF, producing negligible NO, NO_2, NH_3, HCN or DMA.

References

[1] M. Okumura, T. Akita, M. Haruta, X. Wang, O. Kajikawa and O. Okada, Appl. Catal. B 41 (2003) 43.

[2] N.I. Kuznetsova, N.V. Kirillova, L.I. Kuznetsova and V.A. Likholobov, J. Mol. Catal. A 204 (2003) 591.

[3] H. Ehrich, H. Berndt, M.M. Phl, K. Jahnisch and M. Barens, Appl. Catal. A 230 (2002) 271.

[4] N. Herron and C.S. Tolman, J. Am. Chem. Soc. 109 (1987) 2837.

[5] S. Niwa, M. Eswaramoorthy, J. Nair, A. Raj, N. Itoh, H. Shoji, T. Namba and F. Mizukami, Science 295 (2002) 105.

[6] M. Richter, R. Eckelt, B. Parlitz and R. Fricke, Appl. Catal. B 15 (1998) 129.

[7] T. Nanba, C. Kohno, S. Masukawa, J. Uchisawa, N. Nakayama and A. Obuchi, Appl. Catal. B 46 (2003) 353.

[8] J-Oi Uchisawa, A. Obuchi, R. Enomoto, S. Liu, T. Nanba and S. Kushiyama, Appl. Catal. B 26 (2000) 17.

[9] E. Xue, K. Seshan and J.R.H. Ross, Appl. Catal. B 11 (1996) 65.