EFFECT OF ACTIVE METAL-ADDITION ON OXIDATIVE COUPLING OF PHENOL AS A POSSIBLE KEY STEP OF DIOXIN FORMATION OVER deNOx-RELATED CATAYSTS

Shin'ichi Komai, Atsushi Satsuma, Katsuhiro Tokura[1] and <u>Tadashi Hattori</u>

Department of Applied Chemistry, Nagoya University, Chikusa, Nagoya 464-8603, Japan,
[1] Plant R&D Group, Engineering Business Group, NGK Insulators, Ltd., Handa 474-0825, Japan

Introduction

V_2O_5-WO_3/TiO_2 based catalysts, used for the selective catalytic reduction of NOx in waste incineration plants, are also said to be effective for the destruction of PCDD/PCDF[1], and the catalysts are commercially used for simultaneous removal of NOx and PCDD/PCDF. Some engineers, however, suspect on the basis of their experiences that PCDD/PCDF could be formed even over the V_2O_5-WO_3/TiO_2 based catalysts depending on the reaction condition. One of the leading reactions to form PCDD/PCDF is the oxidative coupling of chlorinated phenol[2], and PCDD/PCDF are reported to be easily formed through the coupling of polychlorinated phenols and polychlorinated benzenes over various metal oxides and chlorides[3,4]. It should be noted that the bimolecular reaction such as the coupling becomes especially favourable on solid surface because of the enrichment of reactant molecules through the adsorption. Actually, we reported that the oxide catalysts related to deNOx catalyst, i.e., V_2O_5, WO_3, TiO_2, and V_2O_5/TiO_2, exhibit high catalytic activity for the oxidative coupling of phenol to form dibenzo-p-dioxin (DBD) and dibenzofuran (DBF) shown below[5].
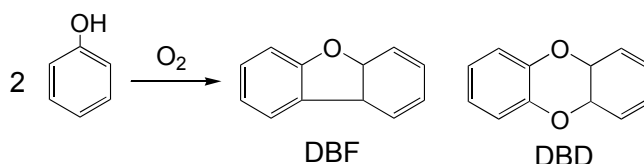
The simultaneous removal of NOx and PCDD/PCDF by V_2O_5-WO_3/TiO_2 based catalysts mentioned above was achieved after the optimisation of catalyst composition, such as an increase in V_2O_5 concentration and an addition of active metal to deNOx catalysts[1]. The purpose of present study is to examine the effect of catalyst components of deNOx catalyst on oxidative coupling of phenol without containing chlorine to form DBF and DBD. The attention has been paid to the catalytically active components, such as V_2O_5 and precious metals.

Methods and Materials

Catalytic activity for oxidative coupling was measured by using a conventional pulse reaction apparatus, details of which were described elsewhere[5]. The apparatus was consisted of a gas chromatograph modified by the introduction of a small reactor between a sample inlet and an analytical column. A small amount ($1mm^3$) of aqueous solution of ca.5% phenol was injected into a flow of a carrier gas, N_2 containing 10% O_2, to be vaporized and carried to the catalyst bed. Unconverted phenol and reaction products were sent to gas chromatograph for analysis. Two series of catalysts were tested in the present study; supported V_2O_5 catalysts and those promoted by Pd and Pt. Two support materials were used. TiO_2 was a Reference Catalyst of Catalysis

Society of Japan (JRC-TIO-4, $50m^2/g$)[6], and SiO_2-TiO_2 was prepared by sol-gel method ($93m^2/g$, Si/Ti = 3/97). Supported V_2O_5 catalysts were prepared by the conventional impregnation method using an oxalic acid solution of NH_4VO_3[6], and Pd and Pt were added to the supported V_2O_5 catalysts thus prepared by a similar procedure using aqueous solutions of $Pd(CH_3COO)_2$ and $Pt(NO_2)_2(NH_3)_2$. The catalysts were calcined at 773 K for 2 h in a flow of air before use.

Results and Discussion
<u>Supported V_2O_5 Catalysts</u>
Table 1 shows the degree of conversion of phenol and the yield of DBF/DBD in the oxidative coupling of phenol over supported V_2O_5 catalysts. The yield was defined as a ratio of 2(DBF+DBD) formed to phenol injected, though, in all the runs in the present report, the amount of DBD formed was much less than that of DBF. When 10mg of catalysts were used, as reported previously[5], the yield was considerably high over V_2O_5/TiO_2 catalyst (entry 1) and low on V_2O_5/SiO_2-TiO_2 (entry 2). It should be mentioned that not only the support but also the V_2O_5 content was different from one another.

The reaction should consist of, at least, three reaction steps: (1) complete oxidation of phenol to COx, (2) oxidative coupling of phenol to DBF/DBD, and (3) complete oxidation of DBF/DBD to COx. It is highly desirable for the present purpose that the step (2) is selectively suppressed and/or the step (3) is selectively enhanced. However, since the conversion on V_2O_5/SiO_2-TiO_2 catalyst was close to the completion, above-mentioned result does not necessarily mean that the V_2O_5/SiO_2-TiO_2 catalyst selectively suppressed the formation of DBF/DBD. It may be possible that high content of V_2O_5 enhanced the catalytic activity in all the steps, leading to the completion of the reaction, i.e., high conversion and low yield.

Table 1 Conversion of phenol and yield of DBF/DBD on supported V_2O_5 catalysts

Entry	Catalyst	Reaction temperature / K			
		473	523	573	623
1	5% V_2O_5/TiO_2 <10mg>				
	Conv./%	78.0	80.5	88.8	93.7
	Yield/%	0.11	0.11	0.03	0.01
2	7% V_2O_5/SiO_2-TiO_2 <10mg>				
	Conv./%	97.5	98.1	99.1	99.7
	Yield/%	0.02	0.02	0.01	0.00
3	5% V_2O_5/TiO_2 <5mg>				
	Conv./%	56.9	61.0	69.5	75.9
	Yield/%	0.10	0.15	0.05	0.02
4	5% V_2O_5/TiO_2 <3mg>				
	Conv./%	44.2	51.4	64.9	89.6
	Yield/%	0.20	0.20	0.10	0.04
5	7% V_2O_5/SiO_2-TiO_2 <3mg>				
	Conv./%	67.5	71.7	81.3	86.5
	Yield/%	0.16	0.15	0.06	0.01

Then, in order to examine the change in the selectivity, catalytic tests were conducted by using smaller amount of catalysts (entries 3-5). As shown, the decrease of catalyst amount resulted in the increase of DBF/DBD yield on both V_2O_5/TiO_2 and V_2O_5/SiO_2-TiO_2 catalysts accompanying the decrease of the conversion, and the yield on V_2O_5/SiO_2-TiO_2 was not essentially different from those on V_2O_5/TiO_2. Thus, it may be concluded that the increase of V_2O_5 content does not selectively suppress the DBF/DBD formation, but high V_2O_5 content unselectively enhances the oxidation activity of all the steps.

Pt- and Pd-promoted V_2O_5 Catalysts
Addition of active metals such as Pd and Pt is known to enhance the oxidation activity, and it is claimed to be effective for the reduction of dioxin formation[1]. Actually, it was proved in our previous study[5] that the addition of active metals such Pd and Pt effectively suppressed the DBD and DBF formation over TiO_2. In the present study, the effect of active metal-addition on the oxidative coupling of phenol over supported V_2O_5 catalysts was examined in the same way as above. In standard condition using 10mg of catalyst, the addition of Pd and Pt to V_2O_5/TiO_2 increased the conversion of phenol, but not remarkably decreased the yield of DBF/DBD (entries

Table 2 Conversion of phenol and yield of DBF/DBD on promoted V_2O_5-based catalysts

Entry	Catalyst	Reaction temperature / K			
		473	523	573	623
1	0.5%Pd/5%V_2O_5/TiO_2 <10mg>				
	Conv./%	87.5	93.8	99.8	100.0
	Yield/%	0.04	0.06	0.00	0.00
2	0.5%Pt/5%V_2O_5/TiO_2 <10mg>				
	Conv./%	91.9	94.6	99.5	99.9
	Yield/%	0.11	0.07	0.00	0.00
3	0.5%Pd/7%V_2O_5/SiO_2-TiO_2 <10mg>				
	Conv./%	93.4	97.2	99.9	99.9
	Yield/%	0.03	0.02	0.00	0.00
4	0.5%Pt/7%V_2O_5/SiO_2-TiO_2 <10mg>				
	Conv./%	96.7	98.3	99.5	99.9
	Yield/%	0.06	0.03	0.02	0.00
5	0.5%Pd/5%V_2O_5/TiO_2 <3mg>				
	Conv./%	67.1	75.4	92.6	99.6
	Yield/%	0.12	0.13	0.03	0.00
6	0.5%Pt/5%V_2O_5/TiO_2 <3mg>				
	Conv./%	59.4	66.2	76.7	85.8
	Yield/%	0.12	0.17	0.05	0.01
7	0.5%Pd/7%V_2O_5/SiO_2-TiO_2 <3mg>				
	Conv./%	76.8	81.9	92.6	98.3
	Yield/%	0.05	0.06	0.03	0.01
8	0.5%Pt/7%V_2O_5/SiO_2-TiO_2 <3mg>				
	Conv./%	65.1	69.6	86.9	94.2
	Yield/%	0.18	0.21	0.08	0.04

1 and 2 in Table 2).   In the case of V_2O_5/SiO_2-TiO_2 (entries 3 and 4), both the conversion and the yield were not so much changed by the addition of Pd and Pt, may be because of too high conversion over unpromoted V_2O_5/SiO_2-TiO_2 catalyst.

In the runs with smaller amount of catalysts (entries 5-8), the conversion was increased in most cases by the addition of Pd and Pt in comparison with the unpromoted catalysts shown in Table 1 (entries 4 and 5). However, the yield of DBF/DBD was not decreased so much in comparison with the yield on the unpromoted catalysts. These results suggest that the addition of Pd and Pt does not selectively suppress the step of DBF/DBD formation, nor selectively enhances the destruction of DBF/DBD.

Figure 1, in which the yield is plotted against the conversion, more clearly shows the effect of Pd- and Pt-addition on the selectivity of DBF/DBD. As shown, the yield decreased with an increase in
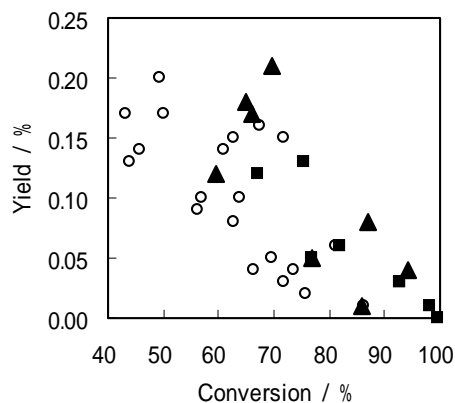

Fig. 1   Effect of Pd- and Pt-addition on the selectivity of DBF/DBD over unpromoted (open circles) and Pd- (closed squares) and Pt- promoted (closed triangles) V_2O_5/TiO_2 and V_2O_5/SiO_2-TiO_2 catalysts. Catalyst amount, 3mg.

the conversion, indicating that DBF/DBD can be destructed with a progress of reaction toward a completion over both promoted and unpromoted catalysts.   However, the difference between both catalysts is obvious: The yield is higher over promoted catalysts than that over unpromoted catalysts. This clearly indicates that the Pd- and Pt-addition reduced the selectivity of DBF/DBD destruction, defined as a ratio of the DBF/DBD destruction to that of whole organic compounds. Thus, it may be concluded that the addition of active metals can suppress DBF/DBD formation through the completion of the overall reaction, but not through the selective suppression of DBF/DBD formation and the selective enhancement of DBF/DBD destruction.

Conclusions
Oxidative coupling of phenol to form DBF/DBD, a possible key step in dioxin formation over deNOx catalysts, was conducted by a pulse method, and the following conclusions were obtained: 1) High content of V_2O_5 and addition of active metals such Pd and Pt effectively suppressed the DBF/DBD formation over deNOx related catalyst. 2) These effects on DBF/DBD formation are due to the enhanced activity of complete oxidation of organic compounds. Or, in other words, dioxin formation could be effectively suppressed only when the catalyst amount is enough to ensure the completion of the reaction.

References
1. Weber, R., Sakurai, T. and Hagenmeier, H.; (1999), Applied Catalysis B: Environmental, 20, 249.
2. Imoto, Y. and Tokura, K.; (1995), Organohalogen Compounds, 19, 459.
3. Kazarek, F.W. and Dickson, L.C.; (1987), Science, 237, 754.
4. Addink, R. and Olie, K.; (1995), Environmental Science and Technology, 29, 1425.
5. Komai, S., Satsuma, A., Tokura, K. and Hattori, T.; (2001), Organohalogen Compounds, 50, 407.
6. Satsuma A., Takenaka S., Tanaka T., Nojima S., Kera Y. and Miyata H.; (1996), Chemistry Letters, 1115; (2002), Applied Catalysis A: General, 232, 93.