FORMATION AND SOURCES I -POSTER

OXIDATIVE COUPLING OF PHENOL: A POSSIBLE KEY STEP OF DIOXIN FORMATION ON deNOx CATALYST

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Introduction

The V_2O_5-WO_3/TiO_2 based catalysts, which are widely used to selectively reduce NOx in the flue gas of municipal waste incineration, are also said to be effective for the destruction of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans[1]. Actually, the catalysts are commercially used for simultaneous removal of NOx and dioxins after the optimization of catalyst composition. On the other hand, it was also reported that dioxins are easily formed from precursors such as polychlorinated phenols and polychlorinated benzenes over various solids, such as metal oxides and chlorides, through surface catalyzed reactions[2].

The present study aims at examining the effect of catalyst component on oxidative coupling of phenol without containing chlorine to form dibenzo-p-dioxin (DBD) and dibenzofuran (DBF) shown below, special attention being paid to the components of deNOx catalysts. It should be
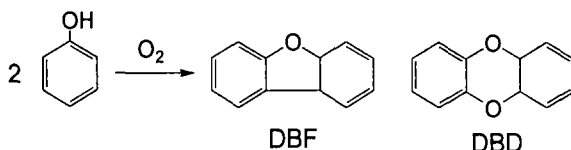
noted that the bimolecular reaction such as the coupling becomes especially favorable on solid surface because of the enrichment of reactant molecules through the adsorption, and that V_2O_5 based catalysts are known to be active for oxidative coupling of benzene derivatives to form anthraquinone, biphenyl and so on[3].

Method and Materials

Catalytic activity for oxidative coupling was measured by using a conventional pulse reaction apparatus, which was consisted of a gas chromatograph modified by the introduction of a small reactor between sample inlet and analytical column as shown in Figure 1. A small amount of catalyst, 10 mg in standard condition, was held by small plugs of quartz wool in Pyrex glass tubing with an inside diameter of 4 mm. The reaction temperature, which was monitored by a thermocouple adjacent to catalyst bed, was raised stepwise every 50 K from 473 K to 623 K. At each reaction temperature, $1 mm^3$ of aqueous solution of 4.98% phenol was injected through a sample inlet by using microsyringe to be vaporized and carried to the catalyst bed accompanying the carrier gas, N_2 containing 10% O_2, with a flow rate of ca. 60 cm^3/min. Unreacted phenol and reaction products were sent to gas chromatograph for analysis, in which a column of 5%DEGS+1%H_3PO_4 on chromosorb WAW DMC was used, after prolonged aging, at a heating rate of 5K/min from 373K to 523K.

Three series of catalysts were used in the present study; unsupported metal oxide catalysts, metal and metal oxide catalysts supported on TiO_2, and deNOx-related catalysts. V_2O_5 and WO_3 were prepared by calcining NH_4VO_3 and $(NH_4)_2WO_4$, respectively, at 773K. TiO_2, also used as the support, was Japan Reference Catalyst (JRC-TIO-4) supplied from Catalysis Society of Japan[4]. The other oxide catalysts were commercially supplied reagents, which were used after being pressed, crushed and then sieved to 28-48 mesh. Supported catalysts were prepared by a conventional impregnation method by using precursors shown in a table of results section. Supported V_2O_5 catalysts were prepared by the procedure described in the reference[5]. The catalyst was calcined at 773 K for 2 h in a flow of air before use.
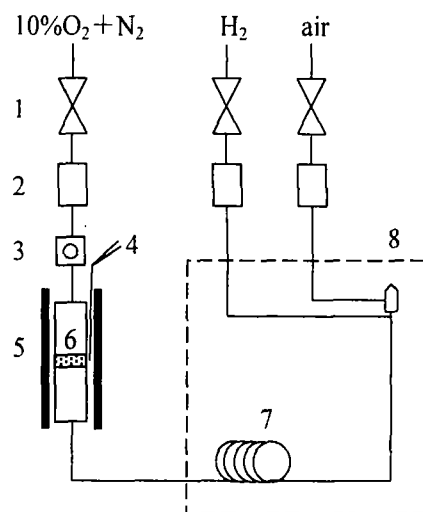

Fig. 1 Pulse reaction apparatus used to measure catalytic activity. 1 stop valve, 2 flow controller, 3 sample inlet, 4 thermocouple, 5 furnace, 6 catalyst bed, 7 column, 8 FID gas chromatograph.

Results and Discussion
Oxide Catalysts Table 1 shows the degree of conversion of phenol and the yield of DBF and DBD on metal oxide catalysts. The yield was defined as a ratio of 2(DBD+DBF) formed to phenol injected. DBF and DBD were formed on most of catalysts, though DBD was significantly less than DBF. The conversion decreased in the following order: TiO_2, MnO_2 > V_2O_5 > WO_3,

Table 1   Conversion of phenol and yield of DBF and DBD on metal oxide catalysts

	Reaction temperature/K					Reaction temperature/K			
	473	523	573	623		473	523	573	623
TiO_2 (50m²/g, JRC-TIO-4[4])					Co_3O_4 (1.2m²/g)				
Conv./%	99.9	81.8	37.1	21.2	Conv./%	-[a]	-[a]	6.1	36.9
Yield/%	0.08	0.23	0.12	0.14	Yield/%	0.30	0.00	0.00	0.00
V_2O_5 (5.4m²/g)					NiO (1.3 m²/g)				
Conv./%	40.7	39.3	59.0	73.6	Conv./%	-[a]	-[a]	-[a]	8.1
Yield/%	1.18	1.19	0.37	0.13	Yield/%	0.00	0.00	0.01	0.05
WO_3 (8.7 m²/g)					CuO (1.1 m²/g)				
Conv./%	33.5	11.7	29.3	38.9	Conv./%	6.9	8.7	22.9	37.8
Yield/%	0.03	0.08	0.12	0.19	Yield/%	0.00	0.15	0.00	0.00
MnO_2 (24 m²/g)					ZnO (4.8 m²/g)				
Conv./%	73.7	98.2	98.2	100.0	Conv./%	15.1	15.6	7.6	24.8
Yield/%	0.16	0.03	0.00	0.00	Yield/%	0.00	0.00	0.00	0.01
Fe_2O_3 (0.5 m²/g)									
Conv./%	-[a]	1.5	-[a]	1.1					
Yield/%	0.35	0.02	0.01	0.09					

[a] Excess amount of phenol was detected due to experimental error of injection amount

$CuO > ZnO > Co_3O_4$, NiO, Fe_2O_3, though high conversion on TiO_2 at lower temperature seemed to be caused by the adsorption, but not by the destruction. This order agrees fairly well with that of surface area given in parenthesis of Table 1. Thus, surface area is suggested to be a key factor to govern the catalytic activity, except for CuO which gave higher conversion than that expected from the surface area. On the other hand, the yield of DBD and DBF did not seem to depend on the surface area so much, but did on chemical property. The yield was the highest on V_2O_5, and relatively high on WO_3 and TiO_2. It should be noted that these are main components of deNOx catalyst.

TiO_2-Supported Catalysts   Table 2 shows the results of catalytic tests of supported catalysts. The addition of small amount of Pd to TiO_2 significantly increased the conversion of phenol and decreased the yield of DBD and DBF in comparison with those on TiO_2. Higher loading resulted in larger effect on both the conversion and the yield. Another run was conducted, by using very small amount of catalyst, to examine the possibility that low yield would be due to high conversion. As shown, low yield was obtained even at low conversion, indicating that the addition of Pd essentially suppress the formation of DBD and DBF. The additions of Pt gave similar results, though experimental error seemed large. Similar effect was obtained by using non-precious metal such as Co, Ni and Cu. Especially, Cu catalyst gave the conversion similar to and the yield lower than Pd and Pt catalysts. All of these results indicate that the addition of active component is effective for the suppression of DBD and DBF formation and for the enhancement of phenol destruction. The DBD and DBF formation, however, was promoted at low temperature by the addition of V_2O_5 to TiO_2, which correspondes to a typical deNOx catalysts.

DeNOx-Related Catalysts   Table 3 summarizes the results on the catalysts related to deNOx catalyst. As mentioned above, some amount of DBD and DBF was formed on TiO_2 and the

Table 2   Conversion of phenol and yield of DBD and DBF on TiO_2-supported catalysts

	Reaction temperature/K					Reaction temperature/K			
	473	523	573	623		473	523	573	623
TiO_2 (JRC-TIO-4[4])					5%Pt/TiO_2 (1.2mg)				
Conv./%	99.9	81.8	37.1	21.2	Conv./%	-[b]	-[b]	4.2	11.1
Yield/%	0.08	0.23	0.12	0.14	Yield/%	0.12	0.02	0.02	0.02
0.5%Pd/TiO_2 [Pd(CH$_3$COO)$_2$][a]					2%Co$_3$O$_4$/TiO_2 [Co(CH$_3$COO)$_2$][a]				
Conv./%	82.0	81.1	98.2	99.7	Conv./%	77.8	74.4	72.0	72.0
Yield/%	0.12	0.07	0.05	0.03	Yield/%	0.01	0.03	0.00	0.00
5%Pd/TiO_2 [Pd(CH$_3$COO)$_2$][a]					2%NiO/TiO_2 [Ni(CH$_3$COO)$_2$][a]				
Conv./%	93.9	99.3	99.9	100.0	Conv./%	70.3	42.7	52.3	65.9
Yield/%	0.00	0.02	0.02	0.02	Yield/%	0.01	0.01	0.01	0.01
0.5%Pd/TiO_2 (1.3mg)					2%CuO/TiO_2 [Cu(CH$_3$COO)$_2$][a]				
Conv./%	35.3	-[b]	21.3	13.2	Conv./%	90.5	90.1	98.3	99.8
Yield/%	0.00	0.04	0.04	0.06	Yield/%	0.00	0.01	0.00	0.00
5%Pt/TiO_2 [Pt(NO$_2$)$_2$(NH$_3$)$_2$][a]					5%V$_2$O$_5$/TiO_2 [NH$_4$VO$_3$][a]				
Conv./%	85.1	94.2	97.7	98.6	Conv./%	64.3	81.5	96.0	100.0
Yield/%	0.64	0.00	0.00	0.00	Yield/%	0.47	0.30	0.09	0.00

[a] Precursor of catalyst component.   [b] See footnote *a* of Table 1.

Table 3   Conversion of phenol and yield of DBD and DBF on deNOx-related catalysts

	Reaction temperature/K					Reaction temperature/K			
	473	523	573	623		473	523	573	623
TiO_2[a] ($50m^2/g$)					$5\%V_2O_5/TiO_2$[a]				
Conv./%	99.9	81.8	37.1	21.2	Conv./%	64.3	81.5	96.0	100.0
Yield/%	0.08	0.23	0.12	0.14	Yield/%	0.47	0.30	0.09	0.00
SiO_2-TiO_2[b] ($100m^2/g$)					$7\%V_2O_5/SiO_2$-TiO_2				
Conv./%	62.3	64.1	59.8	74.5	Conv./%	95.2	97.0	98.6	99.5
Yield/%	0.00	0.00	0.00	0.00	Yield/%	0.03	0.04	0.01	0.00

[a] taken from Table 2 for comparison.   [b] prepared by sol-gel method; Si/Ti=3/97.

addition of V_2O_5 to TiO_2 increased the yield of DBD and DBF at low temperature.   Then, SiO_2-TiO_2, prepared by sol-gel method, was selected as a new support material after screening of support material which was less active for DBD and DBF formation.   As shown, DBD and DBF were not detected in the reaction on SiO_2-TiO_2, which destructed phenol more effectively than TiO_2 maybe due to higher surface area.   Then, V_2O_5 supported on SiO_2-TiO_2, which contained larger amount of V_2O_5 than V_2O_5/TiO_2 because of higher surface area, was prepared and tested. As expected, V_2O_5/SiO_2-TiO_2 was more effective for the conversion of phenol and formed much less amount of DBD and DBF than V_2O_5/TiO_2, which indicates that the modification of the support of deNOx catalyst is effective to suppress the formation of DBD and DBF.

Conclusion
Oxidative coupling of phenol to form DBD and DBF over various catalysts was conducted by pulse method, and the following conclusion was obtained.
1) Principal components of deNOx catalysts, such as V_2O_5, WO_3 and TiO_2, exhibited high activity for the formation of DBD and DBF.
2) The addition of active metals, such as Pd, Pt, Co, Ni and Cu, to TiO_2 suppressed the DBD and DBF formation.
3) The addition of V_2O_5 to TiO_2 enhanced DBD and DBF formation at low temperature, but the use of SiO_2-TiO_2 as the support effectively suppressed the DBD and DBF formation.

References
1. Weber R., Sakurai T. and Hagenmeier H. (1999) Appl. Catal. B 20, 249.
2. Kazarek F.W. and Dickson L.C. (1987) Science 237, 754; Addink R. and Olie K. (1995) Environ. Sci. Technol. 29, 1425.
3. Lars S. and Andersson T. (1986) J. Catal. 98, 138; King S.T. (1991) J. Catal. 131, 215; Zhu J.M. and Andersson T. (1990) J. Catal. 126, 92; Sokolvskii V.D. and Mamedov E.A. (1992) Catal. Today 14, 395.
4. Murakami Y. (1983) in: Stud. Surf. Sci. Catal. 16, 775; Uchijima T. (1991) in: Catalytic Science and Technology vol. 1, Kodansha, VCH, p.393.
5. Satsuma A., Takenaka S., Tanaka T., Nojima S., Kera Y., Miyata H. (1996) Chem. Lett. 1115.