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EFFECTS OF SUPPORTS AND PREPARATION METHODS OF HETEROGENIZED $FeCl_3$ CATALYSTS IN THE OXIDATION OF 3,5-DI-*TERT*-BUTYLCATECHOL IN APROTIC SOLVENTS

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$FeCl_3$-catalyzed oxidation of 3,5-di-t-butylcatechol (DTBC) to 3,5-di-t-butyl-*o*-benzoquinone (DTBQ) by molecular oxygen in tetrahydrofuran (THF) was significantly promoted by addition of SiO_2, γ-Al_2O_3, and active carbon *in situ*. Activity of catalysts prepared by an impregnation method in water or THF was greatly dependent on the supports and solvents used for preparation of the catalysts.

The effect of supports in the heterogenized homogeneous catalysis is rather complex,[1)] but it is important to achieve an enhanced catalytic activity by heterogenation, compared with a homogeneous reaction. Usually the heterogenized catalysts are prepared separately, *e.g.* by an impregnation method, attaching a metal ion or a metal complex to a carrier *via* the formation of chemical bonds or causing the metal species to become physically dispersed within the pore structure of a support,[1,2)] but little has been studied on the effects of supports of catalysts prepared only by mixing the supports and reactants *in situ*.[3)] If the activity of the latter catalysts is as high as or higher than the impregnated catalysts, the convenient method of preparation of catalysts is very useful. We here found a new example which showed an enhanced activity of heterogenized catalysts prepared *in situ*. The reaction we studied is the $FeCl_3$-catalyzed oxidation of DTBC by molecular oxygen, in connection with our previous work,[4)] and the activities of the catalysts were compared with the supported catalysts.

Oxidation of DTBC was performed in a 30 ml flask under an oxygen atmosphere at 25°C. 20 milliliter of dry THF or benzene was used as a solvent, and the solution was stirred magnetically. The reaction was started by adding the solvent containing $FeCl_3$ (0.25 mmol, 0.0406 g) to a mixture of DTBC (1 mmol, 0.2223 g) and support (Catalyst I), or by adding the solvent to a mixture of DTBC and the supported catalyst (9 wt % $FeCl_3$/support). The supported catalysts were prepared by impregnating $FeCl_3$ in water (Catalyst II) or in THF (Catalyst III) on SiO_2, γ-Al_2O_3, active carbon, and some others[5)] at room temperature, and used after drying *in vacuo* at room temperature or at 150°C for 4 h. 1 milliliter aliquots of the reaction solution were diluted with benzene, washed with 2N HCl and water, and analyzed quantitatively by HPLC using biphenyl as an internal reference. The reaction formed selectively DTBQ, and by-products were negligible.

Figure 1 shows the effect of the support/$FeCl_3$ ratio in the reaction using Catalyst I. In the absence of supports, the yield of DTBQ was very low both in THF and benzene (Table 1). The low reactivity in benzene may be partly due to the poor solubility of $FeCl_3$ in benzene. The addition of supports increased the yield of DTBQ. The promoting effect was similar at the low ratio (γ-$Al_2O_3 \gtrsim SiO_2 > C$), but the effect of silica became remarkable at the higher ratio ($SiO_2 > \gamma$-$Al_2O_3 > C$). The addition of carbon over the ratio at 5 was not effective to enhance the activity.

Since the above result suggested that the adsorbed iron species might be more active than unadsorbed $FeCl_3$, the catalytic activities of supported catalysts were studied.

As shown in Table 1, when the reaction was performed with Catalysts II, the further enhanced activity was observed with the silica catalyst. A high activity was observed also in benzene. On the contrary, the activities of the alumina and carbon catalysts were very low. Since the effect of water used for preparation of the impregnated catalysts was striking, the activities of Catalysts III were studied.

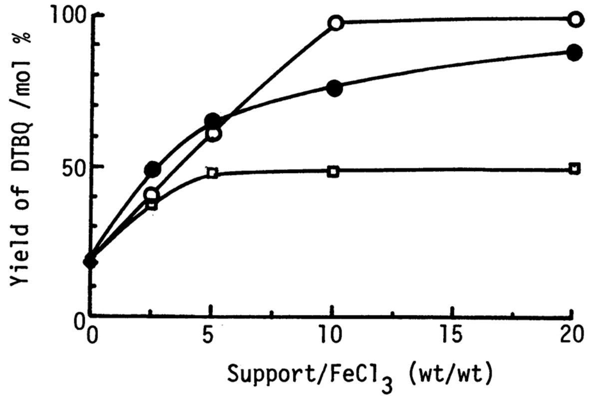

Fig. 1. Effect of the Support/$FeCl_3$ ratio in the oxidation of DTBC in THF. Catalysts were prepared *in situ*. Yield of DTBQ (based on DTBC) was determined after 24 h.
◆:without support; ○:SiO_2
●:γ-Al_2O_3; □:C

For comparison of the activities of Catalysts III with those of Catalysts I and II, the catalysts were dried either at room temperature or at 150°C. The silica catalyst dried at room temperature exhibited the comparable activity with Catalyst I, but the catalyst dried at 150°C was more active than Catalyst II. Interestingly, the alumina catalyst exhibited the similar activity to Catalyst I, and the effect of the drying temperature was small. The carbon catalyst exhibited an intermediate activity between Catalysts I and II, and the activity was lower when the catalyst was dried at a higher temperature.

We have studied effects of some other supports such as SiO_2-Al_2O_3, TiO_2, ZrO_2, Fe_2O_3, Zeolite. Silica-alumina exhibited an intermediate effect between silica and alumina, but activities of the catalysts prepared *in situ* with other supports were less than that of carbon.

The present reaction may be represented, on the whole, by the following equations.

$$2Fe^{3+} + DTBC \rightarrow 2Fe^{2+} + DTBQ + 2H^+ \qquad (1)$$

$$2Fe^{2+} + 2H^+ + \tfrac{1}{2}O_2 \rightarrow 2Fe^{3+} + H_2O \qquad (2)$$

It has been reported that the reaction (1) proceeds stepwise *via* an Fe-DTBC complex and/or a semiquinone radical in an acidic aqueous solution,[6)] but it is not clear at present whether the same mechanism is applicable for the reaction in aprotic

Table 1. Effect of Supports and Preparation Methods of Catalysts in the Oxidation of DTBC[a]

Support	Catalyst[b]	Time (h)	Yield of DTBQ[f] (mol %)
none	I	24	18
	I[e]	24	6
SiO_2	I	5	57
	I	24	98
	II	5	99
	II[e]	24	88
	III[c]	5	54
	III[d]	2	94
γ-Al_2O_3	I	24	76
	II	24	6
	III[c]	24	63
	III[d]	24	71
C	I	24	49
	II	24	7
	III[c]	24	29
	III[d]	24	19

[a] $FeCl_3$(0.25 mmol) + support (0.406 g) or supported catalyst (0.4466 g), DTBC (1 mmol), in 20 ml THF, at 25°C. [b] Catalyst I:prepared *in situ*; II: impregnated in water and dried at 150°C; III: impregnated in THF. [c] Dried at room temperature. [d] Dried at 150°C. [e] Reaction in benzene. [f] Based on DTBC.

Table 2. Adsorption of $FeCl_3$ on Supports and Activities of the Adsorbed $FeCl_3$[a]

Support	Adsorbed $FeCl_3$ (mmol)	Yield of DTBQ (mol %)
SiO_2	0.05	28
γ-Al_2O_3	0.12	35
C	0.15	13

[a] $FeCl_3$ (0.25 mmol) and supports (0.406 g) were stirred for 2 h in 20 ml of THF, filtered, washed with 20 ml of THF, and dried *in vacuo* at room temperature. Reaction was performed with these catalysts. Adsorbed $FeCl_3$ was estimated from the Fe content in the filtrate, which was titrated with EDTA.

solvents. However, it seems very probable that an Fe-DTBC complex, whose structure has not been characterized, is involved as an intermediate.

Table 2 shows the adsorption of $FeCl_3$ on supports in the reaction conditions without DTBC and the activities of the adsorbed $FeCl_3$. The strength of adsorption increases in the order of $SiO_2 << Al_2O_3 < C$, which is reverse to the order of activity of Catalyst I. The yields of DTBQ obtained by the reactions with the adsorbed $FeCl_3$ were less than those with Catalyst I. These results clearly indicate that the enhanced activity of Catalyst I can not be ascribed only to the adsorbed $FeCl_3$. Thus, it seems probable that the Fe-DTBC complex is initially formed with free or weakly adsorbed $FeCl_3$ and the decomposition of the complex to DTBQ is accelerated by the interaction with supports.

On the other hand, it seems also probable that the reaction proceeds on the surface of the supports *via* the Fe-DTBC complex which is formed with the fairly strongly adsorbed iron species. The greatly enhanced activities of the impregnated silica catalysts dried at 150°C indicate that the highly active iron species are formed on the surface. The enhanced activity was not observed with the impregnated alumina and carbon catalysts, but rather the deactivation by water was significant. These results indicate that the activity of the adsorbed iron species is greatly affected by the changes of electronic and/or geometric configurations or the species caused by the bond formation between Fe and supports or by the reaction with water. The low activity of the impregnated carbon catalyst may partly due to the effect of dispersion of the iron species within the pore structure of supports. The result that the highest activity was observed with the silica catalysts suggests that the adsorption of iron species on supports with the moderate strength is important to attain the high activity.

Further studies are necessary for the detailed discussions on the mechanism and reasons for the appearance of the enhanced activities, but the present results indicate that heterogenized homogeneous catalysts should be prepared by way of controlling the above two possible processes.

References

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2) M.S.Scurrell, Catalysis, 2, 215, (1981).

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5) 200 mesh supports were used. Supports were supplied from the Reference Catalysts of Catalyst Society of Japan (SiO_2:JRC-SIO-1, γ-Al_2O_3:JRC-ALO-4, SiO_2-Al_2O_3:JRC-SIAH-1, TiO_2:JRC-TiO-1, Zeolite:JRC-Z-1), Takeda (active carbon:Shirasagi 4-4-6), Merk (Fe_2O_3), and Nakarai (ZrO_2). The effect of the drying temperature of supports was studied with SiO_2 for Catalyst I, and a slight decrease in the activity at higher temperatures (100°∿400°C, *in vacuo*) was observed.

6) E.Mentasti and E.Pelizzetti, J.Chem.Soc.Dalton Trans., 1973, 2605; E.Mentasti, E.Pelizzetti, and G.Saini, *ibid.*, 1973, 2609.

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