CHEMISTRY LETTERS, pp. 1687-1688, 1990.

Palladium Catalyzed Transformation of Benzene to Phenol with Molecular Oxygen

Tetsuro JINTOKU,*† Koichi NISHIMURA,† Ken TAKAKI, and Yuzo FUJIWARA*

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Saijo, Higashi-Hiroshima 724

†Idemitsu Petrochemical Co. Ltd., Tokuyama 745

Very high turnover numbers of the catalyst in direct phenol synthesis from benzene have been attained using palladium catalyst, to give 25% yield of phenol based on the starting benzene.

In previous papers we reported new phenol synthesis from benzene and O_2 via direct activation of an aromatic C-H bond by a $Pd(OAc)_2$/phenanthroline/CO catalyst system.[1] This reaction proceeds under 15 atm of O_2 and 15 atm of CO using a catalyst of $Pd(OAc)_2$ and 1,10-phenanthroline (phen) in the presence of AcOH at 180 °C. However, the turnover number of the catalyst was only 12 and the yield of phenol was ca. 6% based on the starting benzene. We have found that the turnover number dramatically increases up to 100 (25% phenol yield based on benzene) when the catalyst concentration is reduced to 20 mmol%. We wish to report here these results.[2]

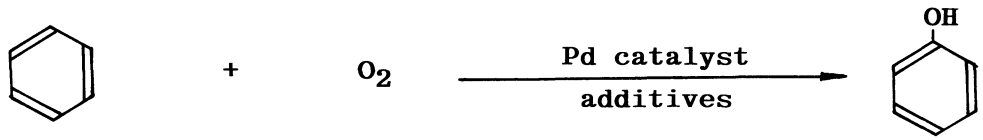

Figure 1 shows the relationship between the phenol yield and the concentration of $Pd(OAc)_2$ catalyst.[3] The reaction was carried out at 180 °C for 3 h in an autoclave charging benzene (8 cm^3), AcOH (2 cm^3), CO (15 atm),[4] O_2 (15 atm) and $Pd(OAc)_2$ and phen (equiv. to $Pd(OAc)_2$, see Fig. 1). One can see that the yield of phenol (based on Pd) increases as decreasing the amount of $Pd(OAc)_2$, and that the yield reaches to more than 10000% (25 % based on benzene) when the concentration of $Pd(OAc)_2$ is 20 mmol%. This remarkable increase of the yield would be attributed to acceleration of

the reoxidation reaction of Pd(0) to Pd(II) by O_2 because of low concentration of the palladium catalyst.[1b] The addition of both CO and phenanthroline is essential to bring about the selective synthesis of phenol. When the reaction is performed without CO and phenanthroline, biphenyl is also formed.[1b] But interestingly enough, the yield of phenol again increases up to 50000% (6.0% yield based on benzene, selectivity 56%) when catalyst concentration is reduced to 1 mmol% as shown in Fig. 2.

The high turnover number (100), yield (25% on benzene), and selectivity (90%) obtained here would make this reaction a practical chemical process which would substitute the cumene process.

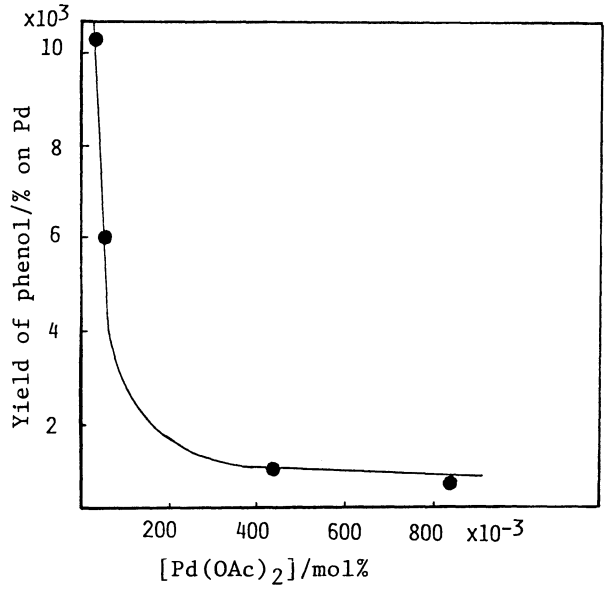

Fig. 1. Plot of phenol yield vs. $Pd(OAc)_2$ concentration. Benzene 8 cm^3, AcOH 2 cm^3, O_2 15 atm, CO 15 atm, $Pd(OAc)_2$/phen=1/1, 180 °C, 3 h.

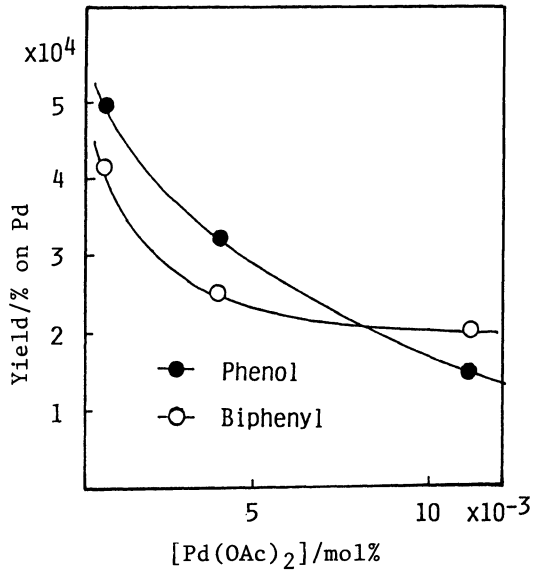

Fig. 2. Plots of yields (● phenol; ○ biphenyl) vs. $Pd(OAc)_2$ concentration. Benzene 8 cm^3, AcOH 2 cm^3, O_2 15 atm, 180 °C, 3 h.

References

1) a) T. Jintoku, H. Taniguchi, and Y. Fujiwara, Chem. Lett., **1987**, 1865; b) T. Jintoku, K. Takaki, Y. Fujiwara, Y. Fuchita, and K. Hiraki, Bull. Chem. Soc. Jpn., **63**, 438 (1990).

2) Presented at the 59th annual meeting of the Chemical Society of Japan: T. Jintoku, K. Nishimura, K. Takaki, and Y. Fujiwara, Abstracts II, p. 1388 (1990).

3) Selectivities of phenol in these cases are 88-90%.

4) CO pressure can be reduced to 5 atm without change in yield and selectivity of phenol.

(Received June 27, 1990)