

Unusual Activity of Carbon Monoxide on Co-Tetraphenylporphyrin supported by TiO₂ for the Reduction of Nitric Oxide

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Carbon monoxide reduces nitric oxide at 50 °C at a much greater rate than hydrogen and very rapidly at 100 °C over Co-TPP-TiO₂ indicating the effective activation of carbon monoxide as well as nitric oxide on the partially reduced Co ion of the supported complex.

We have previously reported that supporting cobalt-tetraphenylporphyrin (Co-TPP) on titania (giving Co-TPP-TiO₂) leads to a strong interaction caused by electron transfer to occur (revealed by u.v. and e.s.r. spectroscopy) providing a significant enhancement of its catalytic activity for the reduction of nitric oxide with hydrogen at moderate reaction temperatures, *ca.* 150 °C.^{1,2} The same catalyst has recently been shown to exhibit much higher activity for the reduction with carbon monoxide. We discuss here some features of the unusual activity of carbon monoxide on Co-TPP-TiO₂.

Co-TPP was synthesized by Adler's method.³ TiO₂, which was prepared from titanium sulphate and calcined at 300 °C after precipitation, was provided by Titan Kogyo (surface area 170 m² g⁻¹). Co-TPP was impregnated on to TiO₂ using a solution in benzene, to give a concentration of 5% w/w. Co-TPP-TiO₂ thus prepared was evacuated at 200 °C for 1 h before the reaction.

The catalytic reaction was investigated at 50 and 100 °C using a circulating reactor (vol. 800 ml; circulation rate 500 ml min⁻¹) with a fixed catalyst bed (4 g), with partial pressures of NO and CO of 100 and 200 mmHg, respectively.

The catalytic activities of Co-TPP-TiO₂ for the reductions of nitric oxide with carbon monoxide and hydrogen at 100 °C

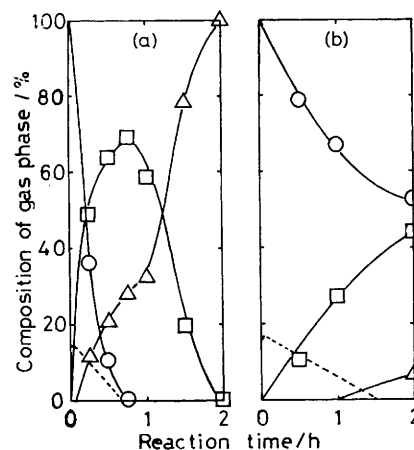


Figure 1. Reduction profile of NO over Co-TPP-TiO₂ at 100 °C. Conditions: pretreatment, catalyst was evacuated at 200 °C for 1 h; partial pressures, NO 100 mmHg, CO or H₂ 200 mmHg; catalyst, Co-TPP-TiO₂ (5 wt%), 4 g. (a) Reduction of NO with CO, (b) reduction of NO with H₂. Composition of gas phase: ○, NO; □, N₂O; △, N₂; --- adsorbed NO.

Table 1. Catalytic activities of Co-TPP and Co-TPP-TiO₂.

Catalyst Reaction temp.	Initial rate ^a	
	Co-TPP-TiO ₂ ^b 100 °C	Co-TPP ^c 250 °C
NO-CO reduction	3.2×10^{-1}	4.3×10^{-3}
NO-H ₂ reduction	1.0×10^{-1}	3.4×10^{-3}
NO decomposition	0.4×10^{-1}	No reaction

^a Rate of N₂O formation [mol (mol Co-TPP)⁻¹ min⁻¹]. ^b Conditions: NO, 50 mmHg; CO or H₂, 100 mmHg; Co-TPP-TiO₂, 4 g; catalyst pretreatment, 1 h evacuation at 200 °C. ^c Conditions: NO, 100 mmHg; CO or H₂, 200 mmHg; Co-TPP, 500 mg; catalyst pretreatment, 1 h evacuation at 250 °C.

are illustrated in Figure 1, where the marked activity of carbon monoxide in comparison with hydrogen is clearly shown. Complete reduction of nitric oxide with carbon monoxide took 45 min, compared with 10 h with hydrogen. No catalytic deactivation after repeated use, with carbon monoxide as reductant, was noted. The reaction appears to proceed in a consecutive manner: *viz.* NO → N₂O → N₂. The reduction of NO with CO proceeded even at 50 °C, although it took 5 days for completion.

The catalytic activities per molecule of Co-TPP for the reduction and decomposition of NO into N₂O on unsupported Co-TPP and Co-TPP-TiO₂ during the initial stages of the reactions are compared in Table 1 to give an estimate of the extent of the activation of the respective substrates caused by supporting. Unsupported Co-TPP showed similar activities for reduction at 250 °C with both hydrogen and carbon monoxide, but no measurable activity for decomposition. Supporting on TiO₂ enhanced the catalytic activity for all reactions examined, the rates being too fast to be measured at 250 °C. The rates for the three reactions differed considerably on Co-TPP-TiO₂, indicating variable extents of activation of the substrates. The highest rate of 3.2×10^{-1} observed at 100 °C with carbon monoxide, three times larger than that with hydrogen, is presumably due to the marked activation of carbon monoxide as well as nitric oxide on the supported Co-TPP.

The activities of the supported catalyst at 250 °C were about 3×10^3 times larger than those of the unsupported one when the activation energy of the former catalyst was taken into account. Supporting on silica gel (surface area 322 m² g⁻¹) led to no activity at 100 °C; however, the activity increased roughly 10-fold at 250 °C probably because of the increase in the effective surface area of Co-TPP,⁴ even if all the molecules of unsupported Co-TPP could adsorb one molecule of nitric oxide at 100 °C. The enhancement due to supporting on TiO₂ (surface area 170 m² g⁻¹) was much larger, thus indicating that there is a second major influence from the support.

The reaction orders of 0.9 in carbon monoxide and zero in nitric oxide suggest the adsorption of both substrates on the central metal ion in Co-TPP. The partially reduced Co ion (postulated as Co^{2-δ} in previous papers^{1,4}) produced on TiO₂ may co-ordinate to the π* orbital of CO to enrich the valence electrons of the carbon atom available to attract the oxygen atom from NO which has itself been adsorbed in the activated bent form. In contrast, hydrogen may be activated by the ligand which is also modified by the support.¹

Thus, the Co-TPP-TiO₂ catalyst may provide an example of strong-support-catalytic species-interactions⁵ which leads to the unusual enhancement of catalytic activity.

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