CHEMISTRY LETTERS, pp. 177-180, 1983.

CATALYTIC ACTIVITY OF Co-TETRAPHENYLPORPHYRIN SUPPORTED ON TiO_2 COMPARABLE TO HOPCALITES FOR THE OXIDATION OF CARBON MONOXIDE AT ROOM TEMPERATURE

Isao MOCHIDA*, Katsuya SUETSUGU[+], Hiroshi FUJITSU
and Kenjiro TAKESHITA

Research Institute of Industrial Science
[+]Department of Molecular Technology
Graduate School of Industrial Sciences
Kyushu University, Kasuga 816

Molecular oxygen oxidized carbon monoxide at 17 °C over Co-TPP-TiO_2 by the rate of 5.3×10^{-3} mmol/g_{cat}·min which was comparable to that of a commercial Hopcalite, indicating very effective activation of carbon monoxide on the partially reduced Co ion of the supported complex to attract an oxygen atom from weakly adsorbed molecular oxygen.

We have previously reported that the supporting of Co-tetraphenylporphyrin (Co-TPP) on TiO_2 (giving Co-TPP-TiO_2) leads to a strong interaction caused by electron transfer to occur (revealed by uv, and esr spectroscopies), providing a significant enhancement of its catalytic activity for the reduction of nitric oxide with hydrogen or carbon monoxide at moderate temperatures around 100 °C.[1,2,3] The unusually high reactivity of carbon monoxide to attract the oxygen atom from nitric oxide at as low as 50 °C stimulates us to study its oxidation with oxygen at room temperature on Co-TPP-TiO_2 in comparison with commercial Hopcalite catalysts.

Co-TPP was synthesized by Adlers' method.[4] TiO_2, which was prepared from titanium oxysulfate and calcined at 300 °C after precipitation, was provided by Titan Kogyo (surface area 156 m^2/g). Co-TPP was impregnated onto TiO_2 using a benzene solution to give a concentration of 5% w/w. Co-TPP-TiO_2, thus prepared, was evacuated at 50 °C or 200 °C before the reaction. Two kinds of Hopcalite catalysts (I,II) were obtained from Nakarai Chemicals Inc. Their compositions are described in the Table.

Table Catalytic Activity of Co-TPP-TiO_2 for the Oxidation of CO with O_2 (17°C)$^{a)}$

Catalysts	CO_2 Formation rate$^{b)}$	Turnover number$^{c)}$
Co-TPP-$TiO_2$$^{d)}$	5.3×10^{-3}	2.1
Co-TPP-$TiO_2$$^{e)}$	2.0×10^{-3}	1.2
Hopcalite(I)$^{f)}$	6.4×10^{-3}	-
Hopcalite(II)$^{g)}$	6.7×10^{-3}	-

a)catalyst:4g, b)mmole/g_{cat}·min, c)converted CO/complex(mole) within 30 min, d)The first run, e)The second run, f)MnO_2(50%), CuO(30%), Co_2O_3(15%), Ag_2O(5%), g)MnO_2(60%), CuO(40%)

The catalytic reaction was carried out at the temperature range of 0 °C and 50 °C, using a circulating reactor (vol. 670 ml; circulation rate, 500 ml/min) with a fixed catalyst bed (4g, placed in the bottom of the vessel connected to the circulating line) with partial pressures of CO and O_2 of 5 and 10 torr, respectively.

The catalytic activities of Co-TPP-TiO_2 for the oxidation of carbon monoxide with oxygen at 17 °C are illustrated in the Figure, where the significant activity of the catalyst at this temperature for the first run is clearly shown. No reaction took place over Co-TPP,TiO_2 nor Co-TPP-SiO_2 at all at this temperature. The activities of commercial Hopcalite catalysts at this temperature are compared to that of Co-TPP-TiO_2 in the Table. The comparable activity of the present catalyst may be remarkable since the only 5% w/w of the catalytic species is present on the surface of TiO_2. Within 30min, the each molecule of the species converted two molecules of carbon monoxide. The catalyst was active even at 0 °C to convert carbon monoxide by the rate of 2.1×10^{-3} mmole/g_{cat}·min. The activation energy in the temperature range between 0 °C and 30 °C was estimated 7.1 kcal/mole. The rate increased scarcely above 30 °C, the diffusion control of the reaction being suspected at the elevated temperatures by the present reactor where the reactant gases flew over the surface of the piled catalyst.

The catalytic activity of the same catalyst in the second run at 17 °C is also illustrated in the Figure. A significant decrease to about a half of the initial activity was observed. This level of activity was maintained for the subsequent runs. The evacuation of the catalyst at 200 °C before the repeated use restored the initial activity, indicating adsorption of some catalyst poisons such as carbon dioxide. The reaction at higher temperatures diminished the retardation.

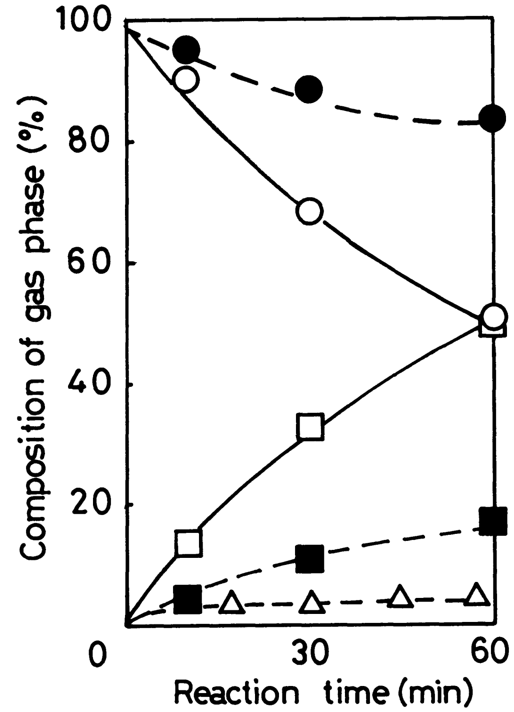

Figure. The catalytic activities of Co-TPP-TiO_2 for the oxidation of carbon monoxide with oxygen at 17°C.
catalyst: 4g, circle: CO,
square: CO_2, triangle: adsorbed CO,
open: first run, closed: second run

The evacuation at 200 °C which has been observed to increase remarkably the activity against the reduction of nitric oxide with carbon monoxide[3] was found to show a little effect on the activity. The CO conversion over the catalyst evacuated at 200 °C was twice of that over the one at 50 °C in the early stage of the reaction (within 10 min), however the same conversion levels were achieved on both catalysts after 30 min. Severe poisoning may take place on the catalyst evacuated at higher temperature in the early stage of the reaction.

The rates under the variable partial pressures of carbon monoxide and oxygen revealed the reaction orders of zero in the former and 0.9 in the latter substrate, suggesting the associative adsorption of both substrates on the central metal ion of Co-TPP and a Langmuir-type reaction mechanism. The adsorption level of carbon monoxide during the reaction is shown in the Figure. The ratio of adsorbed CO/the complex (mole ratio) was ca. 0.2. In contrast, no measurable adsorption of oxygen was detected during the reaction, although oxygen was adsorbed certainly in the absence of carbon monoxide at this temperature. A very low oxidation activity of the catalyst aginst olefins and alcohols in this temperature range may suggest the major importance of activation of carbon monoxide.

Co-TPP supported on TiO_2 calcined at 500 °C showed a very limited activity (ca. one hundredth of Co-TPP on TiO_2 calcined at 300 °C), although its surface area was a half of the latter. This fact suggests that the chemical interaction between the catalyst and the support is the major factor to increase the activity.

The partially reduced Co ion (postulated as $Co^{2-\delta}$ revealed by XPS spectra where the binding energies of Co $2p_{1/2}$ and Co $2p_{3/2}$ were lowered to 795.6 and 780.2 eV from 796.4 and 781.0 eV of the original complex, respectively, by the impregnation on TiO_2) produced on TiO_2 [1,2,3] which survives under oxidation conditions may coordinate to the π^* orbital of ĊO through the back donation to enrich the valance electrons of carbon atom available to attract the oxygen atom from the weakly adsorbed oxygen molecule which may be adsorbed on the same site in the somewhat activated form as nitric oxide. Another oxygen atom left may be very reactive against another molecule of carbon monoxide. Two molecules of nitric oxide can reportedly coordinate onto a cobalt ion of Co-TPP supported on TiO_2[1] as well as Co-TPP[5], supporting the competitive adsorption of CO and O_2 on the same active site.

References

1. I. Mochida, K. Tsuji, K. Suetsugu, H. Fujitsu and K. Takeshita, J. Phys. Chem., 84, 3159 (1980).
2. I. Mochida, K. Suetsugu, H. Fujitsu, K. Takeshita, K. Tsuji, Y. Sagara and A. Ohyoshi, J. Catal., in press.
3. I. Mochida, K. Suetsugu, H. Fujitsu and K. Takeshita, J. C. S. Chem. Commun., 1982, 166.
4. A. D. Adler, F. L. Longo, F. Kampas and J. Kim, J. Inorg. Nucl. Chem., 32, 2443 (1970).
5. B. B. Wayland and J. V. Minkiewiez, J. C. S. Chem. Commun., 1976, 1015.

(Received October 18, 1982)