

dene-2,6-methano-2H-1-benzoxocin-2,7-diol (**12**) was prepared as described above for **9** in 9% (28 mg) yield after chromatography (5% ethyl acetate/petroleum ether). MS, *m/e* (rel. int.), 316 (M^+ , 100), 301 (75), 299 (37), 288 (20), 288 (32), 273 (54), 260 (20), 244 (15), 232 (15), 192 (29); IR (film), 3280, 1620, 1580 cm^{-1} ; NMR (CDCl_3) δ 6.29 (1H, s, arom H), 6.13 (1H, d, $J=2.0$ Hz, arom H), 4.69 (1H, s, OH), 4.30 (1H, brs, C-6H), 2.43 (2H, t, benzylic H), 1.92, 1.67 (2s, 3H each, isopropylidene CH_3 's), 0.87 (3H, t, CH_3).

Preparation of (\pm)-9-(1,1-Dimethylheptyl)-3,4,5,6-tetrahydro-5-isopropylidene-2,6-methano-2H-1-benzoxocin-2,7-diol (13**).** (\pm)-9-(1,1-Dimethylheptyl)-3,4,5,6-tetrahydro-5-isopropylidene-2,6-methano-2H-1-benzoxocin-2,7-diol was prepared as described above for **9** in 18% (65 mg) yield after chromatography (5% ethyl acetate/petroleum ether). (\pm)-9-(1,1-Dimethylheptyl)-3,4,5,6-tetrahydro-5-isopropylidene-2,6-methano-2H-1-benzoxocin-2,7-diol thus obtained was identified by comparison of its spectral data with those published.⁸

Preparation of Cannabigerol (15**)^{2b}.** BF_3 -diethyl ether was added under nitrogen to a stirred suspension of silica (230-400 mesh ASTM) (2 g) in dichloromethane (20 mL). The mixture was stirred for 15 min at room temperature. Geraniol (**14**) (232 mg, 1.75 mmol) and olivetol (**2b**) (180 mg, 1.0 mmol) in dichloromethane (5 mL) were added to the suspension by syringe. The reaction mixture was stirred for 2 days, and was then worked up. The reaction product was separated on silica gel (10% ethyl acetate/petroleum ether) to give 93 mg (29% yield) of cannabigerol. Cannabigerol (**15**) thus obtained was identified by comparison of its spectral data (MS, NMR and IR) with those published or by direct comparison.

Preparation of Cannabigerol dimethylheptyl and Isocannabigerol dimethylheptyl (16** and **17**)⁹.** Under the conditions of procedure (**15**) two compounds were obtained. Cannabigerol dimethylheptyl (**16**) thus obtained was identified by comparison of its spectral data with those published. The first compound eluted was cannabigerol dimethylheptyl (94 mg, 32%), an oil, UV_{max} (EtOH), 273 (ϵ 1260), 280 shnm (1190); MS, *m/e* (rel. int.), 372 (M^+ , 29), 329 (6), 303 (24), 288 (45), 287 (48), 275 (5), 249 (100), 218 (6), 165 (28), 123 (23); IR (film), 3430, 1628, 1584 cm^{-1} ; NMR (CDCl_3), δ 0.85 (3H, t, CH_3), 1.20 (6H, s, $2\times\text{CH}_3$), 1.59, 1.67, 1.80 (9H, s, olefinic CH_3), 3.42 (2H, d, $J=8.0$ Hz, C-8H), 5.04-4.94 (2H, H, m, olefinic h), 6.37 (2H, s, arom H). The second compound eluted was isocannabigerol dimethylheptyl (51 mg, 17%), an oil, UV_{max} (EtOH), 281 nm (ϵ 2610); MS, *m/e* (rel. int.), 372 (M^+ , 31), 287 (78), 249 (22), 177 (33), 163 (31), 151 (67), 147 (31), 81 (28), 69 (100); IR (film), 3370, 1595 cm^{-1} ; NMR (CDCl_3), δ 0.85 (3H, t, CH_3), 1.20 (6H, s, $2\times\text{CH}_3$), 1.34, 1.68, 1.80 (9H, s, olefinic CH_3), 3.47 (2H, d, $J=6.0$ Hz, C-8H), 5.16-4.83 (2H, m, olefinic H), 6.30 (1H, d, $J=2.0$ Hz, arom H), 6.44 (1H, d, $J=3.0$ Hz, arom H).

Acknowledgment. This paper was supported by Joon-san Academic Research Foundation in Wonkwang University, 1994. The authors would like to thank Professor R. Mechoulam and the Department of Natural Products, the Hebrew University of Jerusalem for partial support of this project.

References

- (a) Gaoni, Y.; Mechoulam, R. *J. Am. Chem. Soc.* **1964**, *86*, 1646. (b) Mechoulam, R.; Shvo, Y. *Tetrahedron* **1963**, *19*, 2073.
- (a) Razdan, R. K. *Pharmacol. Rev.* **1986**, *38*, 75. (b) Baek, S. H.; Srebnik, M.; Mechoulam, R. *Tetrahedron Lett.* **1985**, *28*, 1083. (c) Baek, S. H. *Korean J. Med. Chem.* **1993**, *3*, 8. (d) Tius, M. A.; Gu, X-Q.; Kerr, M. A. *J. Chem. Soc. Commun.* **1989**, 62. (e) Huffman, J. W.; Zhang, X.; Wu, M. J.; Joyner, H. H.; Pennington, W. T. *J. Org. Chem.* **1991**, *56*, 1481. (f) Huffman, J. W.; Joyner, H. H.; Lee, M. D.; Jordan, R. D.; Pennington, W. T. *ibid.* **1991**, *56*, 2081. (g) Siegel, C.; Gordon, P. M.; Uliss, D. B.; Handrick, G. R.; Dalzell, H. C.; Razdan, R. K. *ibid.* **1991**, *56*, 6865.
- Yook, C. N.; Baek, S. H.; Cho, S. D.; Park, N. Y. *Bull. Korean Chem. Soc.* **1992**, *13*, 457.
- (a) Cardillo, B.; Merlini, L.; Servi, S. *Tetrahedron Lett.* **1972**, 945. (b) Mechoulam, R.; Yagen, B. *ibid.* **1969**, 5349.
- Razdan, R. K.; Dalzell, H. C.; Handrick, G. R. *J. Am. Chem. Soc.* **1974**, *96*, 5860.
- We warmly thank Prof. R. Mechoulam for kindly providing us with samples of authentic compound (**5**, **7**, **10** and **15**).
- A shorter reaction time gives a similar yield.
- Archer, R. A.; Blanchard, W. B.; Day, W. A.; Johnson, D. W.; Lavagnino, E. R.; Ryan, C. W. *J. Org. Chem.* **1977**, *42*, 2277.
- (a) Gaoni, Y.; Mechoulam, R. *J. Am. Chem. Soc.* **1971**, *93*, 217. (b) Cardillo, G.; Cricchio, R.; Merlini, L. *Tetrahedron* **1968**, *24*, 4825. (c) Zechmeister, L. *Fortschritte der chemie organischer Naturstoffe*: Springer-Verlag: Wien. New York, **1967**, *25*, 175.

Catalytic Oxidation of Carbon Monoxide at Low Temperature over Pd-Cu Loaded Porous Supports

Chul Wee Lee, Seok-Joon Park[†], Young-Sang Kim[†], and Paul Joe Chong*

Solid State Chemistry Lab.,
KRICT, Taejeon 305-606, Korea

[†]Department of Chemistry, Korea University,
Choongnam 339-700, Korea

Received December 2, 1994

The subject of CO removal at low temperature is of practical importance due to its utility in cleaning indoor air pollutants inherent from cigarettes, gas stoves and oil furnaces. To this end, Wacker catalyst (Pd-Cu) has been introduced with some success, for which alumina and carbons are mainly used as supports.^{1,2} The homogeneous Wacker catalyst has been produced commercially for the industrial process of ethylene into acetaldehyde.³

Alternatively, Au-loaded catalysts containing TiO_2 , $\alpha\text{-Fe}_2\text{O}_3$ and Co_3O_4 as supports have been developed for use in low temperature oxidation of CO. However, it is difficult to dis-

perse Au in particulate states through the solid matrices under use, as finely as those of Pt or Pd.⁴ Another catalyst known as Hopcalite⁵ is also commercially available for similar use, which is a mixture of SnO₂, MnO₂, CuO and some other oxides, but being prone to be deactivated by the presence of water vapor.

In this study, Pd-Cu catalysts for CO oxidation at low temperature have been investigated, which are prepared by ion-exchange or impregnation of various supports such as ZSM-5, MS(molecular sieve)-5A, MS-13X, natural zeolite, active carbon and their mixtures. Catalytic performance for each catalyst so prepared has been evaluated in comparison.

Experimental

Sample preparation. The following chemicals were used without further purification: PdCl₂ (Kojima, 98.5%), CuCl₂·2H₂O (Junsei, EP), Cu(NO₃)₂·3H₂O (Junsei, EP), HZSM-5 (SiO₂/Al₂O₃=30, PQ), active carbon (Junsei), MS-5A (Aldrich), Natural Zeolite (Kyung-Ju area in Korea) and MS-13X (Aldrich).

All the catalysts in use were prepared by impregnation of various supports with the aqueous solution of appropriate metallic salts. A typical procedure for loading of 0.89% Pd and 10.5% Cu on active carbon was illustrated as below. A mixed salt solution was prepared from 0.0940 g of CuCl₂·2H₂O and 0.0167 g of PdCl₂, which were dissolved in 25 mL of deionized water at room temperature with stirring for 20 min. Although PdCl₂ itself was insoluble in water, the presence of CuCl₂ enhances its solubility. 0.315 g of Cu(NO₃)₂·3H₂O was then added to the resulting solution, which was stirred until the mixture became homogeneous and colored in dark green. To this solution were added 5 g of support and stirred at 80 °C until complete evaporation of the water. The impregnated catalysts were dried at 70 °C for 3 h, and were kept in a closed container under water vapor saturated at room temperature. All the catalysts were granulated prior to use. They were colored in green, when freshly prepared.

Catalytic activity measurements. The catalytic activity was measured under an atmospheric pressure, employing an apparatus consisting of a flow reactor, which was on-line connected via six-way loop to gas chromatograph (Hitachi 063) with a thermal conductivity detector (TCD). The fixed-bed flow reactor made of pyrex tubings (1.8 cm i.d.; 80 cm long) was externally heated. Each catalyst weighing 0.5 g was placed on sintered glass disc inside the reactor. Reaction temperature was read from thermocouple inserted near the center of the catalyst bed. For the catalytic evaluation the gas mixture made up with 4.0% CO, 20% O₂ and 76% N₂ was used. The total flow rate of the reactant mixture was adjusted to 40 cc/min. Water vapor was supplied *via* by-pass route to feed gases as necessary, prior to their reach of the reactor. The chromatographic column (stainless steel, 3.1 mm o.d.×1.5 m long) was packed with molecular sieve 13 X, by which the reactant and product gases were analyzed at 25 °C. Chromatographic responses were integrated for the catalytic activity in terms of % conversion, as deduced from the difference between the reactor input and output gas samples.

Results and Discussion

Table 1. Catalytic CO conversion of the Pd-Cu catalysts over various supports

No.	Composition (wt. %)	Supports ^a	Conversion %/temperature (°C)				
			20	30	40	50	60
1	0.26Pd-2.95Cu	ZSM-5	3.42	4.47	10.2	19.2	—
2	1+20% A.C.	ZSM-5	4.84	7.25	9.48	12.5	28.0
3	1+50% A.C.	ZSM-5	3.26	14.6	16.9	25.2	31.1
4	0.26Pd-2.38Cu	ZSM-5	5.3	11.7	16.7	11.6	12.5
5	0.2Pd-12Cu	ZSM-5	9.2	13.2	17.1	21.1	29.5
6	2.0Pd-12Cu	A.C.	90.9	91.5	87.6	95.9	95.0
7	2.0Pd-12Cu	A.C.&N.Z. ^c	38.5	69.5	87.4	—	—
8	1.0Pd-12Cu	A.C.	81.0	86.2	90.2	82.0	89.3
9	0.5Pd-12Cu	A.C.	53.3	72.1	74.6	79.5	69.5
10	0.5Pd-12Cu	γ-alumina	6.2	4.4	8.8	—	—
11	0.5Pd-12Cu	MS-5A	3.6	—	10.2	—	21.6
12	0.33Pd-28Cu	A.C.	—	77.1	79.4	—	67.5
13	0.33Pd-39Cu	A.C.	82.8	88.8	—	—	—
14	0.33Pd-56Cu	A.C.	80.3	88.2	90.5	81.3	94.7
15	2.0Pd-12Cu	ZSM-5	—	86.3	—	—	100
16	2.0Pd-12Cu	MS-5A	—	29.3	—	—	—
17	2.0Pd-12Cu	MS-5A+A.C. ^d	—	77.3	—	—	—
18	2.0Pd-12Cu	MS-5A+A.C. ^e	—	88	100	100	—
19	2.0Pd-12Cu	MS-13X	—	14	—	27	94

^aZSM-5; SiO₂/Al₂O₃=30, A.C.=active carbon, N.Z.=natural zeolite, MS-5A=molecular sieve 5A, and MS-13X=molecular sieve 13X. ^bwater vapor feed temperature, 20 °C. ^cweight ratio of A.C. and zeolite is 1:1. ^dweight ratio of MS-5A and A.C. is 7:3.

Pd-Cu catalysts studied in this work were prepared from the homogeneous solution of PdCl₂, CuCl₂·2H₂O and Cu(NO₃)₂·3H₂O by using ion-exchange and/or impregnation, and incipient wetness technique.⁶ It is however indicated that all the preparative methods in use are virtually indistinguishable in catalytic activity.

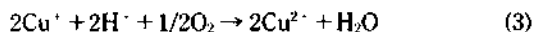
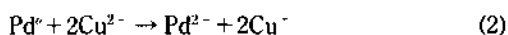
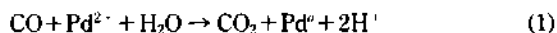
Table 1 shows the performance of Pd-Cu loaded catalysts in comparison with respect to CO oxidation in the range of 20-60 °C. The catalysts were made of various supports such as ZSM-5, MS-5A, MS-13X, natural zeolite, active carbon and their mixtures.

Evidence indicates that the CO oxidation activities mainly depend on the amounts of Pd loadings, being proportional to Pd loading with the same Cu concentration (cf. catalyst nos. 6, 8 and 9 of Table 1). In contrast, the variation of Cu loading alone with equal Pd loadings does not seriously affect the catalytic activity concerned (cf. catalyst nos. 12, 13 and 14 of Table 1). It is however of interest to denote that the relative composition of CuCl₂ and Cu(NO₃)₂ is important for the catalytic activity as well as for the catalytic stability of the Pd-Cu catalyst series. For the effective CO oxidation it is important to streamline the molar ratios of CuCl₂/Cu(NO₃)₂ to the optimum, which are known to be in the range between 3/7 and 4/6, and it was claimed that Cu(NO₃)₂ serves as a promotor when used for CO oxidation.³ All the catalysts used in the current study were prepared within this range.

Among the observed, MS-5A and alumina supported cata-

lysts were found to give the lowest activity (cf. catalyst nos 10 and 11 of Table 1).

It was observed that CO oxidation activity in the presence of water vapor shows higher activity than that in the absence of water vapor as observed by Desai *et al.*¹ Without water vapor, the Pd-Cu catalysts appear to be deactivated quickly by the CO oxidation. In fact this was visually identified by the color change of the catalysts from green to gray. This clearly indicates that a certain amount of water is necessary to maintain the catalytic efficiency. Bearing the importance of water in mind, the CO oxidation mechanism may be postulated as below, in analogy with that of ethylene oxidation in the Wacker process:³



In eqn. (1) above, Pd^{2+} is reduced to Pd^0 by CO, yielding CO_2 . While in eqn. (2) Pd^0 is reoxidized to Pd^{2+} by Cu^{2+} . In eqn. (3), Cu^+ is reoxidized to Cu^{2+} by oxygen. The overall reaction scheme may be simplified as in eqn. (4).

From the above it may be conjectured that the activated metal complexes⁷ are primarily dissolved in surface-hydrated water and the resulting metallic ions then establish the bondings with chemisorbed CO and oxygen species in rather complex manners. In the oxidation of CO, synergism between Pd and Cu is clearly demonstrated. The synergism may be explained by the reversibility of eqn. (2) above for red-ox equilibrium. Espeel *et al.*⁸ in their IR study on adsorption of CO found the simultaneous presence of Cu^+ , Pd^+ and Pd.

It was also found that pretreatment of catalyst with CO tends to enhance the activity of Pd-Cu catalyst toward low temperature CO oxidation, which is similar to the Pt/ SnO_2 catalytic system.^{9,10} While the fresh catalyst of 0.25Pd-2.85 Cu/ZSM-5 shows only 10% CO conversion at 40 °C for catalyst no 1, the catalyst treated with wet CO at 50 °C for 3 h shows about 40% conversion.

Generally it is desirable for catalysts to maintain high activity without significant decay in performance. While for carbon-based catalysts the overall activity profile is retained at least 800 min, the activity of zeolite-based catalysts decreases readily with CO oxidation. This might be explained as follows; since most conventional zeolites have small pore size (<10 Å), the decrease in activity for zeolite-based catalyst is largely due to the pore-filling with water. This will decrease the gas-liquid interfacial surface area.

How can we improve the catalytic activity of zeolite-based catalyst? Zeolite has been known to function as solid solvent, which are able to disperse active metallic ions as surface active species. Active carbon has approximately 100 Å of pore size,¹¹ larger surface area and adsorbing capacity toward water. Hence the addition of carbon to the zeolite can be a simple answer. Physical mixture of carbon and supported catalyst does not increase catalytic activity to a noticeable extent (catalyst nos 1, 2, and 3 of Table 1).

Another evidence supports this answer. It was observed

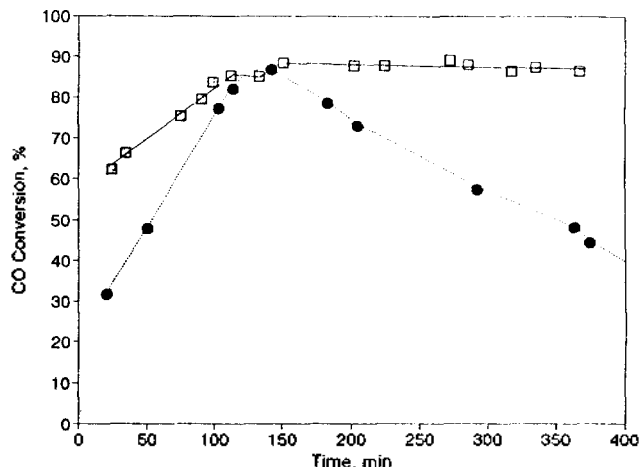


Figure 1. Comparative support effect for 1.6% Pd-10.4% Cu/ZSM-5 (●) and 1.6% Pd-10.4% Cu/active carbon+MS-5A (1:1) (□) at 25 °C as a function of time

that there was no color change of (zeolite+carbon)-based catalysts (green), but only zeolite-based catalyst has changed its color from green to gray during the reaction, indicating the deactivation of the catalyst. As shown in Table 1 (catalyst nos 16, 17, 18 and 6, 7), MS-5A-based catalyst reveals only 29.3% CO conversion, while MS-5A+carbon (7:3) and MS-5A+carbon (5:5)-based catalysts show 77.3 and 88% conversions, respectively. The effect of supports as a function of time is plotted in Figure 1.

Support is another important factor for the catalytic performance. When the stability and regenerability of the catalysts are evaluated, the catalytic activity decreases approximately in the order; active carbon>(active carbon+zeolite)>ZSM-5>MS-13X>MS-5A>alumina.

References

- Desai, M. N.; Butt, J. B.; Dranoff, J. S. *J. Catal.* **1983**, *79*, 95.
- (a) Choi, K. I.; Vannice, M. A. *J. Catal.* **1991**, *127*, 465.
(b) Choi, K. I.; Vannice, M. A. *J. Catal.* **1991**, *131*, 1.
- Lloyd, W. G.; Rowe, D. R. U.S. Patent 3,790,662, 1974.
- Haruta, M.; Tsubota, S.; Kobayashi, T.; Kageyama, H.; Genet, M. J.; Delmon, B. *J. Catal.* **1993**, *144*, 175.
- Brittan, M. I.; Bliss, H.; Walker, C. A. *AIChE J.* **1970**, *16*, 305.
- Palmer, Jr. M. B.; Vannice, M. A. *J. Chem. Tech. Biotechnol.* **1980**, *30*, 205.
- Vargaftik, M. N.; Stromnova, T. A.; Moiseev, I. I. *Russian J. Inorg. Chem.* **1980**, *25*, 127.
- Espeel, P. H.; Tielen, M. C.; Jacobs, P. A. *J. Chem. Soc., Chem. Commun.* **1991**, 669.
- Schryer, D. R.; Upchurch, B. T.; Van Norman, J. D.; Brown, K. G.; Schryer, J. J. *J. Catal.* **1990**, *122*, 193.
- Gardner, S. D.; Hoflund, G. G.; Upchurch, B. T.; Schryer, D. R.; Kielin, E. J.; J. Schryer, J. J. *J. Catal.* **1991**, *129*, 114.
- Breck, D. W. *Zeolite Molecular Sieves*; John Wiley: New York, 1974, p 4.