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CATALYTIC PERFORMANCE OF EGG WHITE TYPE Pt/Al_2O_3 CATALYST IN THE OXIDATION OF C_3H_8 AND CO

Kimio KUNIMORI, Ikuo NAKAJIMA, and Toshio UCHIJIMA
Institute of Materials Science, University of Tsukuba,
Sakura-mura, Ibaraki 305

The egg white type Pt/Al_2O_3 catalyst, without any Pt on the exterior surface, was prepared, and the catalytic activities of C_3H_8 oxidation and CO oxidation were compared with conventional egg shell and uniform type catalysts. For the CO oxidation, it was confirmed experimentally that the egg white type catalyst was more active than the egg shell type at a certain condition.

The distribution of active materials, i.e. metals, in porous supports is known to influence the performance of supported metal catalysts.$^{1)}$ In reactions of positive order kinetics, a given quantity of the metal should be deposited over the exterior of the support in order to minimize diffusion limitations in the porous support,$^{1)}$ and such catalysts (egg shell type) have been usually in commercial use. Recently, Becker and Wei suggested by theoretical calculations that burried layer catalysts with the active ingredient in an egg white or egg yolk position were superior to egg shell or uniform catalysts in both cases of the CO oxidation over Pt which exhibits a negative order kinetics$^{2)}$ and the reaction with pore mouth impurity poisoning.$^{3)}$ Few experimental works concerning the effects of the metal distributions have been reported$^{4)}$ mainly because of difficulty in preparation of the catalysts with the sub-surface metal layers. Becker and Nuttall studied the preparation of the egg white Pt/Al_2O_3 catalysts using the co-impregnation technique.$^{5,6)}$ However, some Pt was invariably present on the Al_2O_3 particle exterior which makes these catalysts unsuitable to study the effect of the metal distributions on reaction characteristics. The aim of this study was to prepare the "ideal" egg white catalysts without any Pt on the exterior surface, and to compare the catalyst performance with that of the conventional egg shell and uniform catalysts in reactions of C_3H_8 oxidation and CO oxidation.

Spherical alumina support pellets (JRC-ALO-3, ca. 3 mm in diameter) from the Japan Reference Catalysts (JRC)$^{7)}$ were used to prepare the Pt/Al_2O_3 catalysts with different Pt concentration profiles as shown in Figures 1 and 2. The preparation method of the egg white catalysts (Nos. 2 and 3) was similar to that of Becker and Nuttall$^{5)}$ except the immobilization process. After the impregnation of the alumina pellets (3 g) with 10 ml of 4 x 10^{-2} mol/l H_2PtCl_6 aqueous solution in the presence of citric acid (CA), the pellets were washed briefly with distilled water, reduced with 30 wt% hydrazine solution for 30 min, and washed again with distilled water. Even in this stage, unreduced Pt ion was present in the exterior layer, as confirmed by coloration with the $SnCl_2$ solution. Therefore, they were treated at room temperature with 0.1 N HCl solution for several hours to remove the unreduced Pt ion, washed with distilled water, dried in air at 110°C, and finally reduced in H_2 at 500°C. Some Pt was deposited on the pellet surface *without the treatment with HCl solution*. The uniform catalyst (No.4) was obtained by co-impregnation with HCl.$^{8)}$ The Pt content of each catalyst was determined by photometric measurement of the Pt concentration of the remaining solution.

The catalytic oxidation was performed with a conventional fixed-bed flow reactor system.$^{9)}$ After a gas mixture of O_2 with N_2 or He was passed downward through the catalyst bed at a fixed temperature for more than 30 min, a reactant gas (C_3H_8 or CO) was introduced to the gas mixture, and the conversion at this temperature was determined. Then, the temperature of the catalyst was varied, while only C_3H_8 or CO was discontinued to flow. The reproducible conversion vs. temperature curve was thus obtained throughout temperature cycle.

C_3H_8 oxidation

The catalysts were pretreated in the reactant gas mixture (C_3H_8 1.0 mol%, O_2 38 mol%, N_2 balance) at 500°C in order to obtain reproducible results.$^{9,10)}$ The sequence of the activity was as follows for the fresh catalysts; egg shell $>$ uniform $>$ egg white, as also shown in Fig.3. It is reasonable from the classical Thiele analysis$^{1)}$, because the kinetics of C_3H_8 oxidation over Pt has a positive first order dependence on C_3H_8 concentration.$^{11)}$ The poisoning experiment demonstrated that the activity of the egg shell catalyst decreased drastically during the poisoning by trimethyl phosphate, and finally became lower than that of the egg white catalyst, as shown in Fig.3. The egg white catalyst is more resistent to the pore mouth poisoning.

CO oxidation

The CO oxidation over Pt has been reported to be structure-insensitive (i.e., the specific activity is constant regardless of the Pt particle size) for higher CO concentration (above ca. 0.2 mol%) such that the rate is inversely proportional to CO concentration.$^{1,12)}$ This means that the activity depends on the percentage exposed of the Pt catalysts. The catalysts were pretreated in air at 700°C for 8 hours so that the activity could be compared at the close level of the percentage exposed. After the pretreatment, the percentage exposed measured by H_2 chemisorption was 9 %, 7 % and 4 % for the egg shell, uniform and egg white catalysts, respectively.$^{13)}$ As shown in Fig.4, the sequence of the activity was determined as egg white $>$ uniform $>$ egg shell. This means that the inner distribution of Pt is more effective in the activity for CO oxidation at a certain condition than the outer distribution. This result is the first experimental evidence of "inversion" in the activity due to the distribution profile; under the diffusion effects, a decline in CO concentration toward the interior of the egg white catalyst can increase the effectiveness factor to above unity owing to the negative order kinetics.$^{1,2)}$ It may be worthy to note that this effect was observed even at relatively low CO concentration (0.3 to 1.3 mol%), as shown in Fig.4. The theoretical prediction was given at higher CO concentration (e.g., ca. 4 mol%),$^{1,2)}$ and it was suggested that the effect was rather small at 1 mol% inlet CO concentration.$^{1)}$

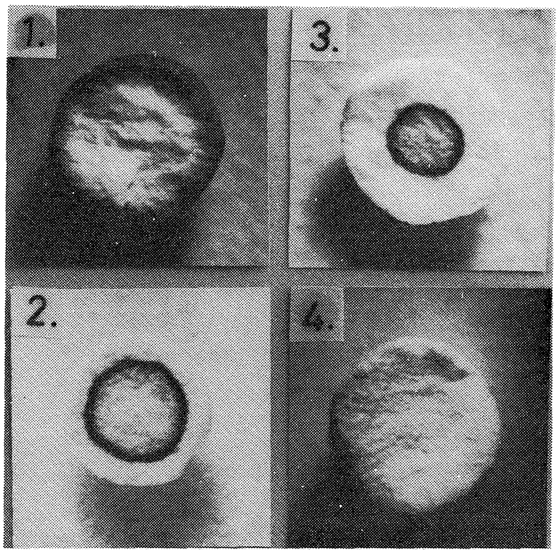

Fig.1. Photographs of the transversal cut section of Pt/Al_2O_3 catalyst pellets. 1. without CA, 2. CA/Pt (molar ratio); 6.8, 3. CA/Pt (molar ratio); 12.1, 4. HCl/Pt (molar ratio); 10.0.

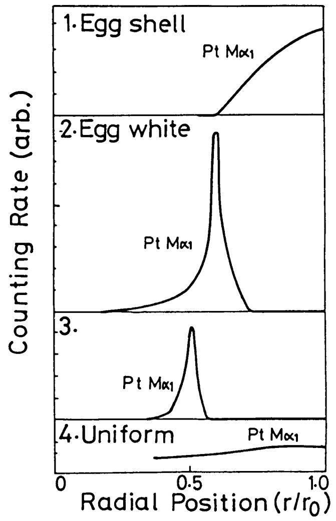

Fig.2. EPMA profiles in the Pt/ Al_2O_3 catalyst pellets. The position at $r/r_0 = 1.0$ means the pellet surface. Numerals in the Figure mean the catalyst numbers in Fig.1.

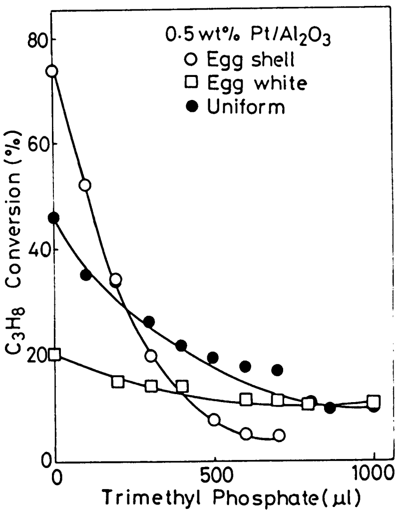

Fig.3. C_3H_8 oxidation at 300°C during the poisoning experiment. SV; 5000 hr^{-1}.

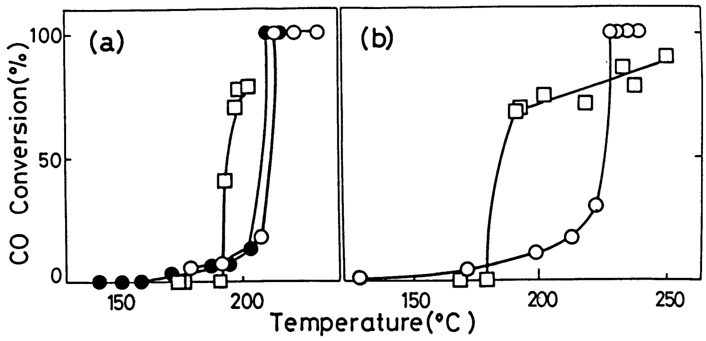

Fig.4. The activities of CO oxidation over the 0.5 wt% Pt/Al_2O_3 catalysts with the different Pt distributions. SV; 8400 hr^{-1}, (a) CO 0.30 mol%, O_2 0.30 mol%, (b) CO 1.30 mol%, O_2 1.47 mol%, (with the balance He). ○ Egg shell □ Egg white ● Uniform

The egg white catalyst in Fig.3 and 4 corresponds to No.2 in Fig.1 and 2.

When the space velocity (SV) of the gas was small (e.g., 1400 hr^{-1}), the activity was the same regardless of the different Pt distribution. At this condition, the light off temperature decreases, where the effectiveness factor should be expected to approach unity.[1,2] More detailed aspects of this work including the effects of SV and the percentage exposed etc. will be reported elsewhere.

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REFERENCES

1) J. Wei and E.R. Becker, Advan. Chem. Ser., 143, 116 (1975).
2) E.R. Becker and J. Wei, J. Catal., 46, 365 (1977).
3) E.R. Becker and J. Wei, J. Catal., 46, 372 (1977).
4) J.C. Summers and L.L. Hegedus, J. Catal., 51, 185 (1978).
5) E.R. Becker and T.A. Nuttall, Preparation of Catalysts II, ed. by B. Delmon et al., Elsevier, p.159 (1979).
6) E. Michalko, U.S. Patent 3259589 (1966).
7) SHOKUBAI(CATALYST), 21, 62 (1979); 22, 110, 115 (1980).
8) R.W. Maatman, Ind. Eng. Chem., 51, 913 (1959).
9) Y. Tokoro, K. Hori, T. Nagira, T. Uchijima, and Y. Yoneda, Nippon Kagaku Kaishi, 1979, 1646 (1979).
10) As for C_3H_8 oxidation over Pt, the specific activity increased proportionally with the increase of the Pt particle size,[9] which means that the catalytic activity is determined only by the Pt distribution regardless of the Pt particle size, since the Pt content was the same (0.5 wt%).
11) Y. Moro-oka, Y. Morikawa, and A. Ozaki, J. Catal., 7, 23 (1967).
12) E. McCarthy, J. Zahradnik, G.C. Kuczynski, and J.J. Carberry, J. Catal., 39, 29 (1975).
13) Before the pretreatment, the percentage exposed was ca. 100 % for the egg shell catalyst, while it was ca. 4 % for the egg white catalyst. In this case, the activity of the former was higher than that of the latter.

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