CHEMISTRY LETTERS, pp. 1749-1750, 1983. © The Chemical Society of Japan 1983

ACCELERATION OF SINTERING BY FORCED REDOX CYCLE

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The effect of redox atmosphere on the sintering of CuO/SiO_2 catalyst was investigated. The sintering was accelerated, when the catalyst was used in catalytic oxidation of ethylene. Further acceleration was observed in the periodic pulse reaction. Redox cycle, especiaaly, forced redox cycle may accelerate the sintering.

Sintering is one of the most important factors of catalyst deactivation and one of the most practical means of fabricating refractory materials. Much attention has been paid to the sintering of precious metal catalysts in the former and to high temperature sintering in the latter. But only a little is known about low temperature sintering of oxide catalysts. Investigating the effect of atmosphere may help to understand the mechanism of sintering and to estimate the life of catalyst in a short term in or near actual reaction condition. In the present letter, we describe that the sintering of CuO/SiO_2 catalyst is accelerated by forced redox cycle.

Catalyst used in the present study was CuO supported on a silica gel, prepared by impregnation of SiO_2 (ID-gel from Fuji-Davison) with an aqueous solution of cupric acetate followed by gradual calcination. CuO content was 20 wt%. The catalyst was treated in the following three conditions: in flowing air, in continuous flow reaction of ethylene oxidation, and in periodic pulse reaction.1) In the second case, a mixture of ethylene, O_2 and N_2 flowed continuously through the catalyst bed. In the last case, a mixture of O_2 and N_2 flowed for a certain duration of time, referred to as pulse width, and then a mixture of ethylene and N_2 flowed for another pulse width. This alternate feed of O_2 and ethylene was repeated cyclically. The sintering of CuO was evaluated by the change of catalytic activity in continuous flow reaction of ethylene oxidation and by the change of amount of chemisorbed NO which can be a measure of active surface area of CuO.2)

The empty marks in Fig. 1 show the change of catalytic activity in various treatments. When the catalyst was treated in flowing air, the catalytic activity decreased rather slowly, as shown by empty squares. When the catalyst was treated in continuous flow reaction, the catalytic activity decreased faster than above, as shown by empty circles. Further acceleration of catalyst deactivation was observed, when the catalyst was treated by the periodic pulse reaction, as shown by empty triangles.

Solid circles and triangles in Fig. 1 represent the change of NO uptake in the continuous flow reaction and in the periodic pulse reaction, respectively. In bose cases, NO uptake decreased in the same extent as the catalytic activity. Particle size of CuO, calculated on the assumption of the stoichiometry of NO/surface Cu = 1, was 60 nm before the treatment, 135 nm after the continuous flow reaction for 170 h, and 265 nm after the periodic pulse reaction for 180 h.

Such deactivation could result from either the deposition of coke or the sintering of CuO particles. However, the former possibility can be neglected in the present case. Because CO_2 could not be detected, when the deactivated catalysts were oxidized in flowing O_2. Thus, the deactivation in the present case resulted from the sintering. The above mentioned results indicate that the sintering of CuO/SiO_2 catalyst is accelerated by ethylene oxidation proceeding on the catalyst, and that the periodic pulse reaction further accelerates the sintering. It is widely accepted that the catalytic oxidation proceeds via the redox cycle.$^{3)}$ Catalyst surface may undergo the microscopic redox cycle in the continuous flow reaction, and the redox cycle may result in the microscopic transport of surface atoms, which accelerates the sintering. In the periodic pulse reaction, O_2 and ethylene were fed alternately. When ethylene is fed, the catalyst is forced to be reduced. And when O_2 is fed, the catalyst undergoes forced oxidation. In this forced reduction-oxidation cycle, the path length of transport of atoms may be longer than that in the continuous flow reaction, which results in further acceleration of sintering.

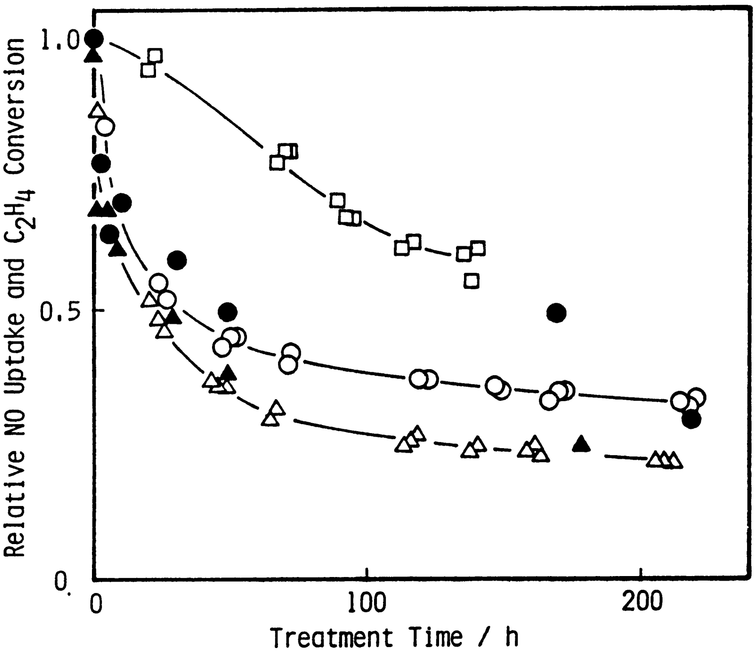

Fig. 1. Changes of NO uptake (solid marks) and conversion of ethylene in catalytic oxidation of ethylene (empty marks) at 563 K. Squares: in flowing air. Circles: in continuous flow reaction, $P_{O_2} = P_{C_2H_4} = 10.6$ kPa, W/F = 0.60 $g \cdot s \cdot cm^{-3}$. Triangles: in periodic pulse reaction, $P_{O_2} = P_{C_2H_4} = 21.3$ kPa, pulse width of O_2 and C_2H_4 = 45 s, W/F = 0.60 $g \cdot s \cdot cm^{-3}$.

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(Received August 4, 1983)