Super Fine Particles and Its Application for Catalysts

Yukuaki MITARAI

Sumitomo Metal Mining Co., Ltd.

INTRODUCTION

It is well known that the properties of solids may be divided into two groups; 1) Structure insensitive, 2) Structure sensitive. Structure insensitive properties are independent of the history of the specimen and of its dimensions. Structure sensitive properties, on the other hand, are directly affected by the factors like the mode of preparation of the specimen, the pre-treatment and the particle size and shape. Examples of structure sensitive properties are the mechanical strength, the actual value of the cohesion, the electric properties, the chemical reactivity and etc. The chemical reactivity, especially the catalytic activity of heterogeneous system, may vary tremendously with different modes of preparation or treatment.

In the field of the catalytic reactions, Boudart[1] also proposed that there are two types

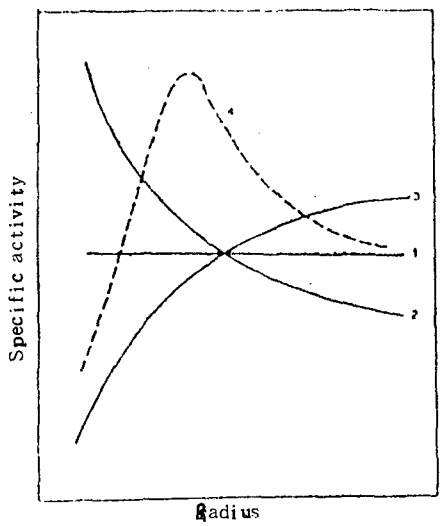


Fig. 1 **Possible forms of dependence of specific activity on particle radius.**

of catalytic reactions termed "Structure sensitive reactions" and "Structure insensitive reactions". Structure sensitive reactions means that changes in the physical properties of a solid, especially particle size of the solid crystallite, should cause changes in its activity and/or selectivity when used as a catalyst. On the contorary, structure insensitive reactions stand for an independent of specific activity and/or selectivity of catalyst on the physical properties of a solid. Fig. 1 shows the examples of the relationship between the specific activity of catalytic reaction and particle size of solid crystallite.

More than 20 years ago, Kubo[2] had predicted that the physical properties of super fine particles of metal should be significantly different from the normal bulk values when the size of the metal particle is less than 10 nm diameter. Afterwards, van Hardeveld et al[3] has revealed the relation between the atomic arrangement of crystal and statistics of surface atoms. In the case of b.c.c crystal lattice (Fig. 2), the existence ratio of atoms depends on the size of crystallite (Fig. 3). The dangling bond of atoms on the faces, the edges and the corner are 1, 2, and 3 respectively. The alangling bond of atom is thought to be closely related to the catalytic reactivity. This report is focused on the relationship between the size of catalyst particle and its catalytic behaviour.

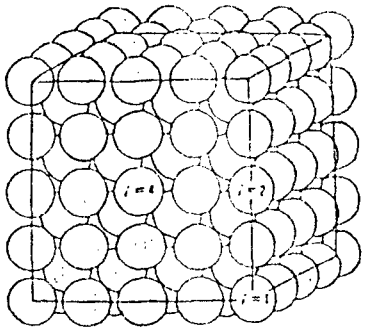


Fig. 2. Atomic arrangement in b.c.c lattice

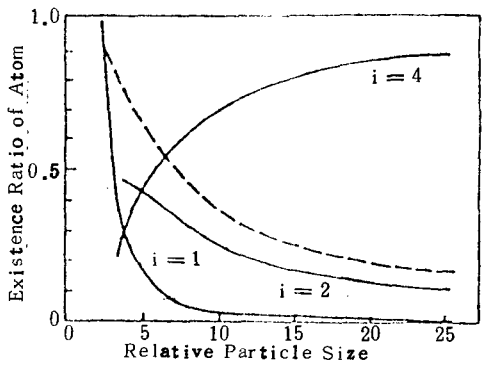


Fig. 3. Statistics of surface atoms.

Structure sensitive reactions

Many studies concerned with the relationship mentioned above have been reported, and only a few examples of reactions, the hydrogenation of ethylene, cyclopropane or benzene on Pt/Al_2O_3 [4] are considered to be structure insensitive reaction. The propane oxidation on Pt/Al_2O_3 (Pt: 2-200 nm) was observed to be a remarkable particle size effect by Tokoro et al[5], however, the specific activity of propane oxidation increased proportionally with an increase of the mean particle size of Pt, this effect was confirmed not to be due to some apparent factors, for examples, the rate control by the boundary layer diffusion or by the micropore diffusion and the increase of effective temperature of the Pt surface.

A lot of reports concerned with the reactions which the specific activity increased with decreasing the particle size of catalyst metal and/or the selectivity changed with its particle size have been published. This size effect is said to be a typical particle size effect of super fine particle and also one of the structure sensitive reactions. Carter et al[6] studied the effect of Ni crystallite size on the catalytic activity of Ni/SiO_2-Al_2O_3 using ethene hydrogenolysis, and found that the specific catalytic activity of Ni rapidly increased with a decrease in the particle size when it was less than 5 nm diameter (Fig. 4). It was found by Anderson et al[7] that the rate of the hydrogenolysis of n-hexane on ultra thin film catalyst increased with decreasing

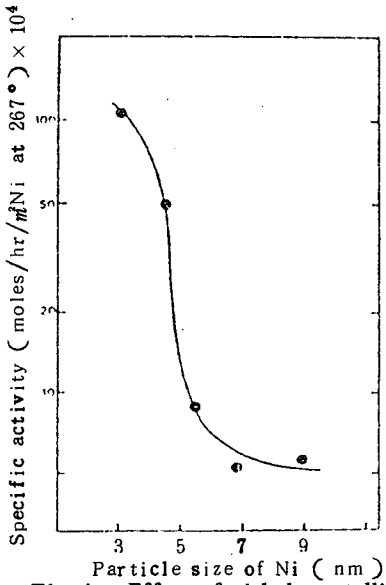


Fig. 4. Effect of nickel crystallite size on specific catalytic activity for ethane.

Pt crystallite size in the range of 1.5-4 nm (Table 1). Recently Ueno et al[8] have reported the effect of metal particle size on the activity and the selectivity of hydrogenation of propionaldehyde. They adopted a excellent techniques to control metal particle size and prepared Ni/SiO_2 catalyst by hydrolysis of mixed solution of ethyl silicate and nickel hydroxide dissolved in ethylene glycol.

Table 1. Hydrogenolysis of -2-methylpentane at 273°C

	1	2	3	4	5	6
UTF: 0.02	(15	--	0.7	36	-	-
UTF: 0.04	(15	-	0.6	19	-	-
UTF: 0.08	20	29	0.8	5.8	29	5.2
UTF: 0.5	38	130	1.4	3.5	14	1.9
UTF: 1.0	43	163	2.1	9.0	13	1.7
UTF: 2.5	58	265	3.9	5.2	8.5	1.3
thick film	-	300	2.2	7.5	5.0	0.5
0.8% Pt/SiO_2	-	-	2.5	5.4	-	-

($\mu g/cm^2$)

1. average Pt crystollite diameter (A)
2. total Pt surface area (cm^2)
3. max. conversion (%)
4. proportion (%) reacting by hydrogenotysis
5. Initial hydrogenolysis rate (10^m mole, $S^{-1}.cm^{-1}$)
6. steady hydrogenolysis rate (10^m mole, $S^{-1}.cm^{-1}$)

The hydrogenation of propionaldehyde generally accompanies decomposition of the aldehyde as follow.

$$CH_3CH_2CHO + H_2 \begin{cases} \rightarrow CH_3CH_2CH_2OH \\ \rightarrow C_2H_6 + CO + H_2 \end{cases}$$

The specific activity of formation of propyl alcohol and the selectivity of the reaction were simultaneously investigated. During the reaction of propionaldehyde with hydrogen on the

catalyst, hydrogenation may occured on the metal atoms located at the corners or edges of the crystallite, while the decomposition of the aldehyde may take place on the metal atoms located on the plane face of the crystallite, because the curve of the selectivity of propyl alcohol formation closely coincided with the curve of the fraction the corners atoms and the edges atoms of Ni crysallite (Table 2, Fig. 5, Fig. 6, Fig. 7). Takasaki et al[9] reported similar results obtained from the decomposition of 1-propanol on Rh/SiO_2.

Table 2. Summary of Ni particle-size results measured by TEM and SAXS

Catalyst no	[NI] (%)	2Rc/Å	2Rn/Å	SAXS/Å result	half-width/Å	TEM/Å result
1	2.2	38	30	20	18	25
2	4.3	57	41	30	19	40
3	9.2	87	81	70	20	60
4	12.4	105	95	85	30	75
5	25.5	120	114	105	25	95

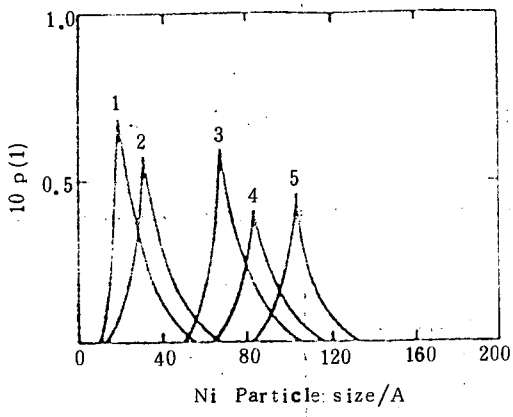


Fig. 5. Particle-size distribution of Ni in Ni/SiO_2 catalysis reduce by H_2 at 450°C for 4H

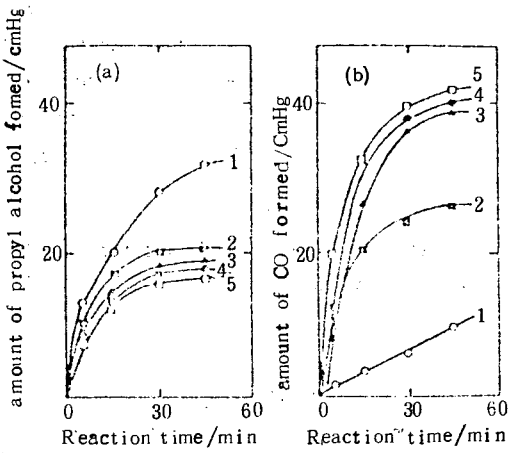


Fig. 6. Formation of propyl alcohol (a) and cabbon monoxide (b) per unit mass of Ni in the the catalysis

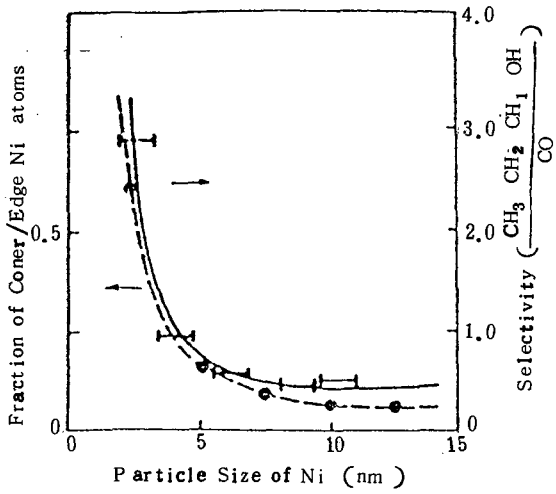
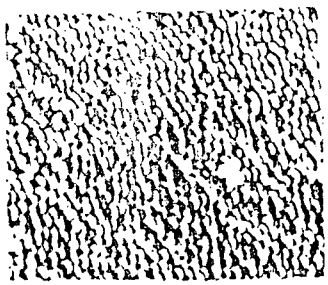


FIg. 7. Relation between selectivity reaction and particle size.

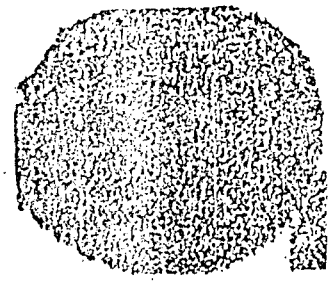
Catalyst support preparation

Trials to produce the catalyst support consist of super fine particle were done in our laboratory[10]. In order to prepare the support containing completely uniform and monodispersed particles, the hydrolysis of metal alkoxide by water/alcohol solution was carried out and carefully controlled the conditions of the formation of metal oxide nuclei and the growth of the oxide. Scanning electron micrographs of TiO_2 obtained by this method are shown Photo 1 and Photo 2. It was found that not only primary particles but also secondary particles were extremely uniform and well dispersed and the average crystallite size was in the range of 5-10 nm.



2μ

Photo. 1 SEM Observation of TiO_2



100μ

Photo. 2 SEM Observation of TiO_2 (Inner Structure)

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