PARTICLE SIZE EFFECT AND STRUCTURE SENSITIVITY IN CATALYSIS BY SUPPORTED METAL CATALYSTS

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Keywords: Catalytic Reaction, Supported Metal Catalyst, Particle Size Effect, Structure Sensitivity, Metal Dispersion

Introduction

The activity of supported metal catalysts is influenced by the size of metal particles in different fashions. The turnover frequency, *TOF*, has been used as a specific activity of a catalyst, and mostly it is an average value because the catalyst has different types of active sites. A few efforts have been made to express the distribution of various active sites in terms of the distribution of activation energy of desorption of probe gas molecules (Seebauer, 1994; Arai *et al.*, 1995, 1996). For practical supported metal catalysts, however, it is still difficult to specify the type of working active sites, so the significance of the average *TOF* remains unchanged. The particle size effects have been investigated by examining the relation of *TOF* and the size of metal particles (*R*) or the degree of metal dispersion (*D*). This relation has been examined by many researchers, and results obtained so far have been reviewed by several authors (Che and Bennett, 1989; Bond 1991; Ponc and Bond, 1995).

Farin and Avnir (1988, 1989) attempted to describe the particle size effects by an expression of

$$\log TOF = \log k + (D_R - 2)\log R \quad (1)$$

where *k* is a constant and *D_R* is reaction dimension, a measure of structure sensitivity. They examined the literature data and found several cases of catalytic reactions in which a logarithmic plot of *TOF* vs. *R* was linear. Although Eq. (1) is a phenomenological expression and one can find in the literature other cases where the *TOF* vs. *R* plot is not linear, the basic idea is useful.

1. Modification of Farin and Avnir's Equation

We think, however, that it is better to modify Eq. (1) by using *D* instead of *R* as follows.

$$\log TOF = \log TOF^* + n \log D \quad (2)$$

where *TOF** and *n* are constants. One can use *n* to measure the degree of structure sensitivity. When *n*=0 for catalytic reaction, it is structure-insensitive. When *n* is not equal to 0, it is positively or negatively structure-

Fig. 1 Logarithmic plot of *TOF* against *D* for *n*-butane hydrogenolysis at 433 K over 0.5% Ru/SiO₂ catalysts (Bond, 1991)

sensitive and the degree of sensitivity is represented by *n*. The absolute value and sign of *n* are both able to describe the structure sensitivity. Another constant, *TOF**, has a clear meaning in that it is *TOF* at an extreme of *D*=1, in contrast to *k* of Eq. (1). When *D*=1, the supported metal exists as two-dimensional islands, for which the influence of support should be the strongest. So, it would be more helpful to use *TOF** to see the influence of support compared to *TOF* with *D*<1 for three-dimensional metal particles.

2. Application of Modified Equation

The following will give a few examples that are analyzed and discussed with *n* and *TOF**. **Figure 1** gives the results on *n*-butane hydrogenolysis at 433 K over 0.5% Ru/SiO₂ catalysts (Bond, 1991). The catalysts were prepared from RuCl₃, one through direct reduction to Ru (Cat I) and another through oxidation to RuO₂ followed by reduction to Ru (Cat II). Figure 1 shows that the reaction is positively structure-sensitive for Cat I and Cat II catalysts but the degree of structure sensitivity is larger for Cat I than for Cat II. This suggests that the distribution of working active sites on Ru particles depends on the method of preparation, being different between Cat I and Cat II. However, Cat I and Cat II give very similar *TOF**

* Received on April 15, 1997.

Fig. 2 Logarithmic plot of TOF against D for n -butane hydrogenolysis at 433 K over 1% and 4% Ru catalysts supported on Al_2O_3 (Bond and Slaa, 1994)

values, indicating that the activity of two dimensional Ru islands is not influenced by the method of preparation.

Figure 2 shows the results of n -butane hydrogenolysis at 433 K over 1% and 4% Ru/ Al_2O_3 catalysts (Bond and Slaa, 1994). Before the activity measurement, they were subjected to three different pretreatments: HTR1, reduction with H_2 at 753 K; O/LTR, oxidation with air at 623 K followed by reduction with H_2 at a lower temperature of 433 K; HTR2, reduction with H_2 at 753 K following O/LTR. Figure 2 indicates that the structure sensitivity is negative, in contrast to the above case with Ru/ SiO_2 , and the structure sensitivity depends on the pretreatment but not on the amount of Ru loaded. Very similar TOF^* values are obtained with Ru/ Al_2O_3 catalysts as well, but they are smaller than the TOF^* value with Ru/ SiO_2 catalysts (see Fig. 1).

It is generally recognized that the dependence of TOF on D may be explained by the changes of geometric and electronic properties of active metal particles (Bond, 1991; Poncet and Bond, 1995). These properties change with various preparation variables including metal precursors, pretreatment conditions, and support materials. So one can see various types of structure sensitivity in the literature and they are not easy to account for. For the above cases of n -butane hydrogenolysis over Ru catalysts, the structure sensitivity is different between SiO_2 and Al_2O_3 supports. The structure sensitivity is expected to be similar if the support merely influences the size of Ru particles. A possible explanation is that the electronic state of Ru particles on Al_2O_3 is different from Ru/ SiO_2 due to the presence of some residual $Ru^{\delta+}$ species (Bond and Slaa, 1994) and the formation of an Al-Ru alloy. These would result in the difference of structure sensitivity between SiO_2 and Al_2O_3 supports. The formation of an Al-Pt alloy was reported for Pt/ Al_2O_3 catalysts (Den Otter and Dautzenberg, 1978).

In **Fig. 3** our results on hydrogenation of acetonitrile

Fig. 3 Logarithmic plot of TOF against D for hydrogenation of acetonitrile (AN) at 383 K and benzonitrile (BN) at 503 K over 5% Ni catalysts on various supports (Rode *et al.*, 1997)

trile (AN) and benzonitrile (BN) over 5% Ni catalysts on various supports including SiO_2 (SI), $SiO_2 \cdot Al_2O_3$ (SA), Al_2O_3 (AL), and TiO_2 (TI) (Rode *et al.*, 1997) are presented. The catalysts were prepared through hydrogen reduction at 673 K except Ni/ TiO_2 with lower Ni dispersion reduced at 773 K. The results with different supports are correlated by one line for either AN or BN. It is shown that the structure sensitivity is negative and the degrees of structure sensitivity are similar for the hydrogenation of AN at 383 K and BN at 503 K. The range of D is not sufficient for the estimation of TOF^* . However, it seems as a first approximation that the TOF^* value little depends on the supports used in these Ni-catalyzed hydrogenations, indicating that they have a simple effect changing the size of Ni particles. The activities did not correlate to electronic properties of Ni particles measured by X-ray photoelectron spectroscopy, so geometric properties are an important factor responsible for the observed dependence of TOF on D . It was suggested that the adsorption of nitriles was influenced by the surface geometric properties of Ni particles (Rode *et al.*, 1997).

For acetonitrile hydrogenation over Fe/MgO catalysts, Bond and Stone (1996) indicated a simple correlation between the rate of reaction and the total surface area of Fe particles. So this reaction is structure-insensitive. Several other structure-insensitive reactions are reported in the literature, for example, carbon monoxide hydrogenation by Pd and benzene hydrogenation by Ni (Somorjai, 1981; Boudart and Djéga-Mariadassou, 1984).

Conclusion

A phenomenological expression is presented to describe the influence of particle size on the activity of supported metal catalysts. This expression has been applied to a few examples, and we have discussed the particle size sensitivity and the effects of preparation vari-

ables on the catalytic activities. Eq.(2) may be useful for the analysis of a few aspects of catalysis by supported metal particles.

Nomenclature

D	= degree of metal dispersion or fraction exposed	[—]
D_R	= reaction dimension in Eq. (1)	[—]
k	= constant in Eq. (1)	[—]
n	= constant in Eq. (2), degree of structure sensitivity	[—]
R	= size of metal particles	[m]
TOF	= turnover frequency	[s ⁻¹]
TOF^*	= turnover frequency at extreme of $D=1$	[s ⁻¹]

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