Turnover Frequency (TOF) for Insight into Reaction Rates via Noble Metal Supported Catalysts

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Abstract:

Turnover frequency (TOF) refers to the number of reacted molecules per surface active site per time for a catalytic reaction. Today, rate data in arbitrary units or plots of conversion versus time are slowly becoming the exception rather than the rule in the scientific literature of catalysis. With only one unit, a value of TOF offers a straightforward way to compare data obtained in different laboratories. In the present work, we show TOF measurement approach and insight into noble metal supported catalysis it provides.

1 Introduction

The reaction rate or rate of reaction is the speed at which reactants are converted into products. which plays an very importance role in catalytic reactions. Chemical kinetics is the part of physical chemistry that studies reaction rates. The concepts of chemical kinetics are applied in many disciplines, such as chemical engineering, enzymology and environmental engineering. According to IUPAC Gold Book definition, the reaction rate for a chemical reaction occurring in a closed system under isobaric conditions, without a build-up of reaction intermediates, is defined as Eq. (1).

$$r = \frac{reacted\ amount}{reaction\ time\ \times\ reaction\ zone} \tag{1}$$

Thus basically, a reaction rate is reacted amount per time per zone, whereas reaction amount typically refers to mole of a chemical, while time could be hours or second. [1, 2, 3, 4] It varies a lot, however, for the selection of reaction zone, e.g. the most commonly used volume, mass, and surface area. The unit of reaction rate accordingly varies. For example, $mol \cdot s^{-1} \cdot m^{-3}$ is typically used for a reaction occurred in a batch reactor. [5, 6]

In the field of heterogeneous catalysis, especially over supported catalysts, The reaction rate in these arbitrary units cannot provide insight into a catalyzed reaction. Instead turnover frequency (or turnover rate) is more often used. [7, 8, 9, 10, 11] In the present paper, we will introduce concepts related to turnover frequency, metal dispersion and their measurement approach.

2 Metal Dispersion

Dispersion is mostly used for metal supported catalysts, as defined by Eq.(2), although it could well be extended to other catalyst types.

$$D = \frac{N_S}{N_T} \tag{2}$$

The dispersion, i.e. the fraction of surface atoms, is usually between 0 and 1 (or 0 and 100%). Chemisorption measurements give direct measurement of the number of surface atoms (see next section) however, in the case of spherical particles, D can also be deduced using the relations between D and the specific surface area or the mean particle size. [12, 13, 14] For spherical particles, useful relationships between metal dispersion, surface area and mean particle diameter can be established by making assumptions on the nature of the crystal planes exposed on the metal surface. [15, 16, 17, 18, 19] Thus, assuming equal proportions of the three low-index planes (111), (100) and (110) on the poly-crystalline surface of a face-centered cubic (fcc) metal, it is easy to calculate, from crystal data, the number of atoms per unit area in these planes and the mean number of atoms n_s. [20, 21]

3 Chemisorption and H_2-O_2 Titration

Selective chemisorption (i.e. formation of an irreversibly adsorbed monolayer) is the most frequently used method for characterizing supported metallic catalysts. [22, 23] The measurement of a gas adsorbed selectively on the metal at monolayer coverage provides the metal surface area and metal dispersion, if the stoichiometric coefficient of the reaction of chemisorption is known. [24, 25, 26] Hydrogen chemisorption as a probe for metal dispersion has been reviewed in detail in the literature [27, 28]. The proposed reaction is as follows:

$$Pt \ + \ 0.5H_2 \longrightarrow Pt - H \tag{3}$$

Hydrogen - oxygen titration (H_2-O_2 titration) was introduced in 1965 by Benson and Boudart for alumina-supported platinum catalysts [29].

The proposed reactions are as follows:

$$Pt \ + \ 0.5O_2 \longrightarrow Pt - O \tag{4}$$

$$Pt - O \ + \ 1.5H_2 \longrightarrow Pt - H \ + \ H_2O \tag{5}$$

Thus the overall reaction is shown below:

$$Pt \ + \ 1.5H_2 \ + \ 0.5O_2 \longrightarrow Pt - H \ + \ H_2O \tag{6}$$

As compared to Eq. (3), Eq. (6) provides three-times higher sensitivity, leading to the reason for its widely and commonly usage. [30, 31, 32, 33, 34]

4 Intrinsic Kinetics

The major advantage of using intrinsic reaction kinetics is that these are scale independent, in contrast with the often-used, so-called apparent kinetics, which still include the effects of transport phenomena. [35, 36, 37, 38, 39] Therefore the effects from (disturbing) transport phenomena have to be separated from the chemical reactions. Thus reliable kinetic rate expressions are a prerequisite for safe and economical reactor design. [40, 41] More information can be found in our prior publications and literature for how to exclude mass and heat transfer effects on catalytic reactions.

5 TOF Calculations

As discussed above, TOF is calculated after intrinsic kinetics (excluding mass and heat transfer effects on catalytic reactions), metal dispersion of supported metals are obtained. The unit of TOF is typically s^{-1}, which varies from 0.01-10 s^{-1}. [42, 43] Using TOF over various supported noble metal catalysts, reaction rate is comparable, providing more insight into the nature of catalytic reactions. It is, however, unfortunate that only several metals are good candidates (Pt, Pd, Ru, Rh, etc.) for this approach, because of the accuracy of metal dispersion measurements. [13, 44, 45] A well-known exclusive example is gold (Au) supported catalyst, since it does not adsorb H_2 molecules.

6 Concluding Remarks

In the present work, detailed approaches of chemisorption and H_2-O_2 titration, metal dispersion, intrinsic kinetics and TOF calculations are discussed and compared. It is concluded that accurate measurement of TOF plays an important role in evaluating a catalyst or a whole catalytic system.

7 Acknowledgments

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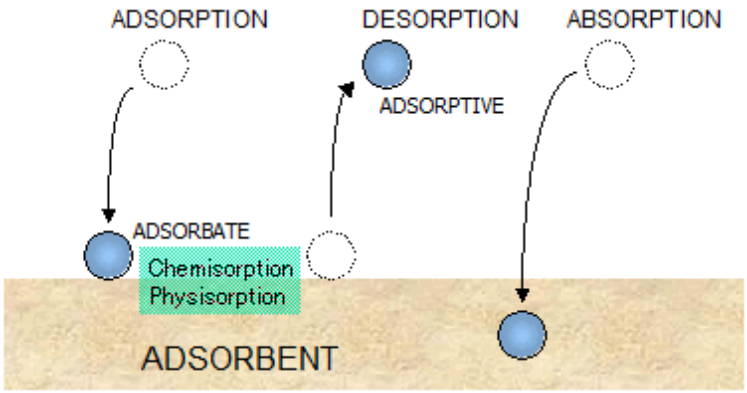

Figure 1: Comparison of Physisorption and Chemisorption

Turnover Frequency (TOF) for Insight into Reaction Rates via Noble Metal Supported Catalysts

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Catalog: ***Catalytic Performance***
