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Supplementary Information

Highly dispersed Pd nanoparticle on SiO_2 support for dehydrogenation of Liquid Organic Hydrogen Carriers

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1. **Calculation of metal particle sizes**
2. **Kinetic parameter calculations**
3. **Calculation of Turnover frequency (TOF)**

1. Calculation of metal particle sizes

The particle sizes were calculated based CO pulse adsorption experiments using following equations[1]. The specific surface area A (m^2/g) is given by:

$$A = \frac{nV_m N_A a_m}{22414 \cdot m}$$

where, n is the stoichiometric coefficient, V_m the chemisorption volume (cm^3), N_A the Avogadro's number (6.02×10^{23} mol^{-1}), a_m the metal cross-section area of an atom (m^2), m the metal mass of the sample (g).

The metal particle size D_m (m) could then be calculated by:

$$D_m = \frac{6}{\rho A}$$

where ρ represents the metal density (g/m^3).

2. Kinetic parameter calculations

The kinetic parameters of 0.3%Pd-NH_2(1) and 0.3%Pd-IM were calculated in this study. The dehydrogenation process of 12H-NECZ can be divided into the following three elementary reactions:[2, 3]

$$12H-NECZ \xrightarrow{k_1} 8H-NECZ + 2H_2$$

$$8H-NECZ \xrightarrow{k_2} 4H-NECZ + 2H_2$$

$$4H-NECZ \xrightarrow{k_3} NECZ + 2H_2$$

where k_1, k_2, and k_3 represent rate constants of three elementary reactions. All three reactions were reported to follow first-order kinetics[4, 5]. According to previous research, the reaction kinetics can also be approximated by the formation rate of 4H-NECZ in the following form:[6, 7]

$$r_1 = -\frac{dC_{12H-NECZ}}{dt} = k_1 C_{12H-NECZ}$$

$$r_2 \approx \frac{dC_{4H-NECZ}}{dt} = k_2 C_{4H-NECZ}$$

$$r_3 = \frac{dC_{NECZ}}{dt} = k_3 C_{NECZ}$$

These expressions could be integrated to obtain the analytical solutions. The rate constants were obtained by fitting with experimental results. The relationship between rate constants and temperature was described by Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}}$$

where A is the pre-exponential factor and E_a is the activation energy.

3. Calculation of turnover frequency (TOF)

In this study, turnover frequency (TOF) for H_2 generation was calculated to demonstrate the reactivity difference of catalysts for each reaction steps. TOF for H_2 generation were defined as the amount of H_2 produced per active site in unit time. Specifically, TOF_t is the total amount of H_2 produced on one active site per minute in 12H-NECZ dehydrogenation process. TOF_1, TOF_2, and TOF_3 are the amounts of H_2 produced per active site per minute in the three elementary dehydrogenation reactions: 12H-NECZ to 8H-NECZ (TOF_1), 8H-NECZ to 4H-NECZ (TOF_2), 4H-NECZ to NECZ (TOF_3).

TOF_t was calculated based on the total amount of H_2 released during the reaction process within the first hour using the following expression:

$$TOF_t = \frac{amount\ of\ H_2\ released}{catalyst\ metal\ amount \times metal\ dispersion \times reaction\ time}$$

TOF_1, TOF_2, and TOF_3 were calculated based on the product distribution of 8H-NECZ, 4H-NECZ and NECZ:

$$TOF_1 = TOF_t \times \frac{2 \times amount\ of\ consumed\ 12H-NECZ}{amount\ of\ H_2 release}$$

$$TOF_3 = TOF_t \times \frac{2 \times amount\ of\ produced\ NECZ}{amount\ of\ H_2\ released}$$

$$TOF_2 = TOF_t - TOF_1 - TOF_3$$

References

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