Hydro-demethylation mechanism of toluene over Pt catalyst by DFT calculations

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Abstract: To clarify the hydro-demethylation mechanism of toluene over Pt catalyst, the surface energy of Pt facets and the adsorption and demethylation energies of toluene were investigated by DFT calculations. The surface energy calculations revealed that the coordinative unsaturation facets, such as Pt(311) and Pt(331) facets, might appear by the increase in the Pt particle size. Toluene adsorption and demethylation energy calculations indicated that the demethylation energy was lower than the adsorption energy on Pt(311) and Pt(110) facets. Therefore, demethylation of the adsorbed toluene easily proceeded using the adsorbed hydrogen over these coordinative unsaturation facets, such as Pt(311) and Pt(110) facets.

Keywords: Organic hydride, DFT calculation, Pt unsaturated facet.

1. Introduction

Hydrogen is a prospective secondary energy source. Although hydrogen is currently stored as a compressed gas, it is ineffective and difficult to handle because it needs high pressures. Organic hydride method is one of the efficient methods to store and transport hydrogen. This method uses a hydrogenation-dehydrogenation cycle reversibly between naphthene and aromatic compounds, such as methylcyclohexane (MCH) and toluene. MCH is the most suitable candidate for organic hydride because of its wide temperature range within which it can exist as a liquiform material (178-373 K). Although Pt/Al_2O_3 catalyst showed high activity for dehydrogenation of MCH, the catalyst also produced methane and benzene as byproducts by hydro-demethylation. Produced methane leads the decrease in the purity of hydrogen and benzene is a carcinogenic material. To suppress these byproducts, it is important to clarify the hydro-demethylation mechanism of MCH. Hydro-demethylation might occur by the reaction between produced toluene and hydrogen over the Pt catalyst. Therefore, we investigated the hydro-demethylation mechanism of toluene over Pt exposed facets by DFT calculations.

2. Theoretical

For the surface energy calculations, DFT wave basis pseudopotential calculation was performed using the CASTEP code. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation (XC) functional, and ultrasoft pseudopotentials were used. The plane-wave cutoff energy was taken as 300 eV. The Monkhorst-Pack k point separation in the reciprocal space was set to approximately 0.04 $Å^{-1}$. For the all calculations, an fcc bulk and a slab model of Pt were designed. The number of layers in the slab model is used when the total energy increment of the n-layer slab is 0.05 eV or under. The vacuum space is 20 Å with both sides. Surface energy (γ_{hkl}) is calculated from Eq. (1) using the energy of bulk (E_{bulk}) [eV], the energy of an n-layer slab ($E_{n\text{-}slab}$) [eV], the number of atoms in the slab model (n), and the surface area (S) [$Å^2$]. From the calculated surface energy, the structure of Pt particle is estimated applying the Wulff theorem[1].

$$\gamma_{hkl} = (E_{n\text{-}slab} - nE_{bulk})/2S \tag{1}$$

For the toluene adsorption and demethylation energy calculations, DFT all-electron calculation was performed using DMol^3 code. The GGA with PBE XC functional and DFT Semicore pseudopotentials were used. The Monkhorst-Pack k point separation in the reciprocal space was set to approximately 0.04 Å^{-1}. The wave functions are expanded in terms of double-numerical with polarization functions basis set with real-space cutoff of 4.5 Å. The number of layers in the slab model is three or four and the lower two layers are fixed. The vacuum space is 15 Å. In the all calculations, the spin-polarization was examined because Pt has paramagnetism.

3. Results and discussion

Table 1. Calculated surface energy of each Pt facet.

Pt facet	Surface energy γ / eV Å^{-2}	γ_{hkl} / γ_{111} / -
(100)	0.1175	1.17
(110)	0.1266	1.26
(111)	0.0966	1.00
(210)	0.1264	1.31
(211)	0.1126	1.12
(221)	0.1080	1.07
(310)	0.1250	1.29
(311)	0.1178	1.17
(320)	0.1255	1.24
(321)	0.1175	1.16
(322)	0.1064	1.06
(331)	0.1486	1.47
(332)	0.1037	1.07

The surface energy of each Pt facet was calculated (Table 1). From the calculated surface energy, the structure of Pt particle was estimated. The coordinative unsaturation facets might appear by the increase in the Pt particle size. When the Pt particle size was smaller than 5 nm, only Pt(111) and Pt(100) facets, which are the terrace facets, could exist. When the Pt particle size was 5 nm or larger, the Pt(311) and Pt(331) facets, which are the step facets, existed on the particle[2] (Figure 1).

Figure 2 shows energy diagram of toluene demethylation on Pt(111), Pt(100), Pt(311) and Pt(110) facets. From Fig. 2, the adsorption energy was the largest on Pt(110) facet and the least on Pt(111) facet. The demethylation energy was higher than the adsorption energy when toluene adsorbed on Pt(111) facet. The demethylation energy was almost the same as the adsorption energy on Pt(100) facet. On the other hand, the demethylation energy was lower than the adsorption energy on Pt(311) and Pt(110) facets. Therefore, the demethylation of toluene could easily proceed without desorption of the formed toluene over Pt(311) and Pt(110) facets (Figure 2). Furthermore, Pt atoms on Pt(111) and Pt(100) facets rise to adsorbed toluene more largely than on Pt(311) and Pt(110) facets at the transition state.

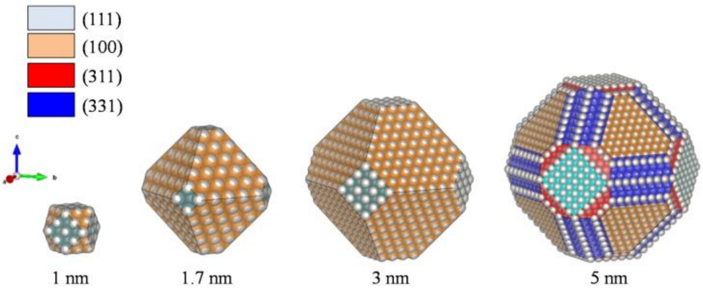

Figure 1. Calculated optimized structure of Pt particle.

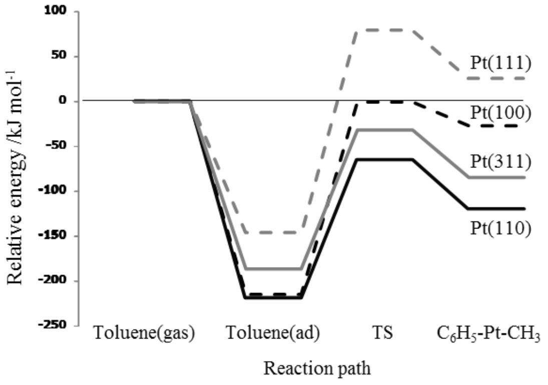

Figure 2. Energy diagram of toluene demethylation.

4. Conclusions

The surface energy calculations indicated that the coordinative unsaturation facets, such as Pt(311) and Pt(331) facets, might exist by the increase in the Pt particle size. Toluene adsorption and demethylation energy calculations suggested that the demethylation energy was lower than the adsorption energy when toluene adsorbed on Pt(311) and Pt(110) facets. Therefore, demethylation of toluene could easily proceed over these coordinative unsaturation facets which exist on the large Pt particle.

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References

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