行政院原子能委員會
委託研究計畫研究報告

【太陽能及乙醇/氫氣轉換之量子化學計算模擬及實驗驗證】

【Quatum Simulations of Solar Energy and Ethanol to Hydrogen Conversion Processes with Experimental Validations】

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中文摘要

本計畫是為期三年行政院原子能委員會委託研究計畫之第二年執行結果摘要。這一年主要的工作在進行以下兩個目標：1. 利用大型電腦計算解釋 InN/TiO_2 太陽能電池的製作機制及 InN 與 TiO_2 之間利用量子點及有效的化學鍵製作方法。2. 理論與實驗驗證 L. D. Schmidt 的 Rh/CeO_2 乙醇轉換氫氣催化劑的性能，並進而研究發現新而便宜的催化劑。

在乙醇轉換氫的實驗上，Schmidt 的 Rh/CeO_2 實驗結果已完全證實用乙醇與水的混合物目前已得到 115%的轉換率，實驗比較粉狀、方型與棍狀的 CeO_2 奈米結晶效率的差異已完成，且研究 CeO_2 與 ZrO_2 混合氧化物的實驗已在進行中。

大型量子計算可分為三方面，1. 乙醇轉氫在不同催化劑表面反應基制的研究。2. 量子點在 TiO_2 表面吸附的能量與結構。3. 發展 SCC-DFTB 應用於乙醇轉氫及量子點/TiO_2 方面的大型計算。

在乙醇轉氫方面的計算，今年主要在了解水氣轉氫 ($CO+H_2O \rightarrow CO_2+H_2$) 在 Rh/$CeO_2$ 上的反應機制及能量。也進行乙醇在 Rh/CeO_2/ZrO_2 催化劑上的吸附及分解，同時，CuO/Al_2O_3 對乙醇轉氫的可行性也在計算中。

在量子點/TiO_2 系統的計算，今年著重於$(InN)_x$/TiO_2 及$(Si)_x$/ TiO_2 兩系統的研究，量子點的大小影響 TiO_2 帶隙的計算，已供給良好的結果。

在 SCC-DFTB 程式的發展，目前也有很好的進展，這個程式的完成，將可供給本計算團隊用 VASP 及 CASTEP 以外作大型分子群的計算。

除了上述的計算外，$In(CH_3)_3$ 與 HN_3、NH_3、HO_2 及 H_2S 的氣相反應機制及能量變化已計算完畢，此系列的反應，與 InN、InO_x 及 InS_x 的沉積有關。

Abstract

This is the report for the second of the 3-year research project on the computational and experimental studies of the InN/TiO_2 system and/or the catalytic conversion of ethanol to hydrogen by Schmidt's technique employing the Rh/CeO_2 catalyst. Our goals are two-fold: 1. Utilization of the large scale computation to elucidate processes relevant to the InN/TiO_2 solar cell system including quantum-dot and chemical functional-group modifications of the $InN\text{-}TiO_2$ interface; 2. Experimental and computational studies of Schmidt's ethanol to H_2 conversion processes in order to search for cheaper and equally efficient catalysts.

For the ethanol to H_2 conversion studies, Schmidt's Rh/CeO_2 catalytic conversion data have been fully duplicated with up to 115% conversion from autothermal oxidation with mixtures of C_2H_5OH and H_2O. Studies have been completed on different nanocrystal forms of CeO_2 (powder, cube and rod) on the efficiency of the H_2 conversion; conversions greater than 125% have been reached using the rod form of the catalyst.

Computationally, we have focused on three aspects: 1. Catalytic conversion of ethanol to H_2; 2. Electronic structures of quantum dots (QDs) attached to TiO_2 nanoparticles; 3. Development of the SCC-DFTB (self-consistent charge-density functional theory tight-binding) method for large cluster calculations.

For the ethanol to hydrogen conversion related calculations, we have studied the H_2O+CO water-gas shift reaction on the Rh/CeO_2 catalyst. The reaction was found to be obeying the

Langmuir-Hinshelwood mechanism through chemisorption of both H_2O and CO on Rh (for CO) and/or Ce (for H_2O) sites, followed by the dissociation of H_2O(a) and oxidation of CO(a) by HO(a). In addition, calculations for adsorption and decomposition of ethanol on Rh/CeO_2-ZrO_2 and CuO/Al_2O_3 have been done.

For the QD/TiO_2 related calculations, focus has been made on $(InN)_n/TiO_2$ (n=1-3) and $(Si)_x/ TiO_2$ (x=1-67). The effects of QD-sizes on the system's band gap have been clearly elucidated.

For the development of the SCC-DFTB method, a basic code for the establishment of elemental parameters has been completed, and the effort on the conversion of binding properties of key elements such as Ti, B, Cl, Si, ….among others is being made.

Aside from the aforementioned large practical systems, we have also carried out detailed potential energy surfaces for reactions of $In(CH_3)_3$ with HN_3, NH_3, HO_2 and H_2S in the gas phase. These reactions may take place in the OMCVD of the corresponding QDs.