TiO_2 负载的 Pd_4 催化剂上 CO 氧化偶联制 DMO 的理论研究

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草酸二甲酯（DMO）作为一种重要化工原料，广泛应用于加氢制乙二醇[1]。CO氧化偶联是DMO合成的主要方法，Pd是这一过程中有效的催化剂。由于Pd是贵金属，极大的限制了其大规模工业化生产，因此如何减少Pd的用量且保持其高催化活性成为我们研究的重点。将贵金属高分散性地负载在载体上，不仅能减少贵金属的用量，而且还可以提高催化剂的催化活性[2]。采用密度泛函理论（DFT）方法对CO氧化偶联在完美和缺陷TiO_2(001)表面负载的Pd_4催化剂上的反应进行了研究。结果表明：在这两种催化剂上有两条反应路径：CO-$COOCH_3$和$COOCH_3$-$COOCH_3$偶联路径，其中$COOCH_3$-$COOCH_3$偶联是最优路径。通过比较最优路径的决速步骤能垒发现，缺陷TiO_2(001)表面负载的Pd_4催化剂对CO氧化偶联制DMO反应表现出更高的催化活性。这表明Pd_4/TiO_2-O_v不仅减少了Pd催化剂的用量，并且保持着较好催化活性。

关键词： CO氧化偶联制DMO；Pd_4/TiO_2；Pd_4/TiO_2-O_v；DFT

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CO Oxidative Coupling to DMO over Pd_4 Supported on TiO_2 Catalyst: A DFT Study

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DMO as an important raw material is widely used in hydrogenation to ethylene glycol, and CO oxidative coupling to DMO is the crucial step. Pd is an effective catalyst for this reaction. However, the large-scale industrial production is greatly restricted due to its expensive price. Therefore, how to reduce the amount of Pd and maintain its high catalytic activity has become the focus of our research. In this work, the mechanism of CO oxidative coupling to DMO was studied on both perfect and defective TiO_2(001) surfaces supporting Pd_4 cluster by DFT calculation. The results show that the defective TiO_2(001) supporting Pd_4 cluster shows better catalytic activity by comparing the energy barrier of rate determining step, which implies that Pd_4/TiO_2-O_v not only reduces the amount of Pd catalyst, but also has a high catalytic activity.

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