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TEM Study on Catalyst Deactivation during Selective Acetylene Hydrogenation

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Pd/Al_2O_3 catalysts are used for selective acetylene hydrogenation and may deactivate via the accumulation of hydrocarbons (so-called green oil). Previously we observed that green oil completely covers the surface of the used catalyst, blocking active sites and raising many of the Pd particles off the alumina support [1]. Due to its practical importance, the process of green oil formation has been studied extensively by both industrial and academic researchers [1, 2]. However, most of the previous studies have focused on the effect of green oil on reaction kinetics, overlooking the generation and growth process. This is partly due to the long time required for green oil to form and the lack of *in situ* observation techniques to monitor the process. We are current employing *in situ* and *ex situ* TEM to follow the process of green oil formation on the surface of the active catalyst.

To study green oil formation it is necessary to determine suitable reactor conditions that accelerate its formation. We loaded pre-reduced 0.1% Pd/Al_2O_3 catalysts into a micro reactor which was then run at temperatures and reactant gas concentrations higher than real applications to speed up green oil formation. Four different reactant gas mixtures, representing the major components of the industrial feedstock, were tested in an effort to probe the mechanism for green oil formation and its composition. The mixtures were: 1) C_2H_4; 2) $50\%C_2H_4+ 50\%H_2$; 3) C_2H_2; 4) $50\%C_2H_2+ 50\%H_2$. The reaction was run for 5 hours at a pressure of 600 Torr and 100°C and the samples examined by TEM to look for evidence of hydrocarbon formation.

Figures a-d are typical TEM images of the samples after removal from the reactor and show that green oil has formed on the surfaces of the catalyst. We find that C_2H_4 doesn't give rise to green oil by itself [Fig.a] or combined with H_2 [Fig.b]. In contrast, C_2H_2 leads to green oil formation by itself [Fig.c], contrary to the general belief that H_2 has to be involved. The hydrocarbon was formed around each Pd particles proving definitely that it is metal particles and not the support that give rise to green oil formation. The green oil around the metal particles will overflow in time to cover the entire support as shown previously [1]. Most Pd particles are pushed off the support (in agreement with results from the industrial reactor [1]) presumably by the green oil originating between metal-support interface. The early stages of this lift-off process will be studied by *in-situ* ETEM.

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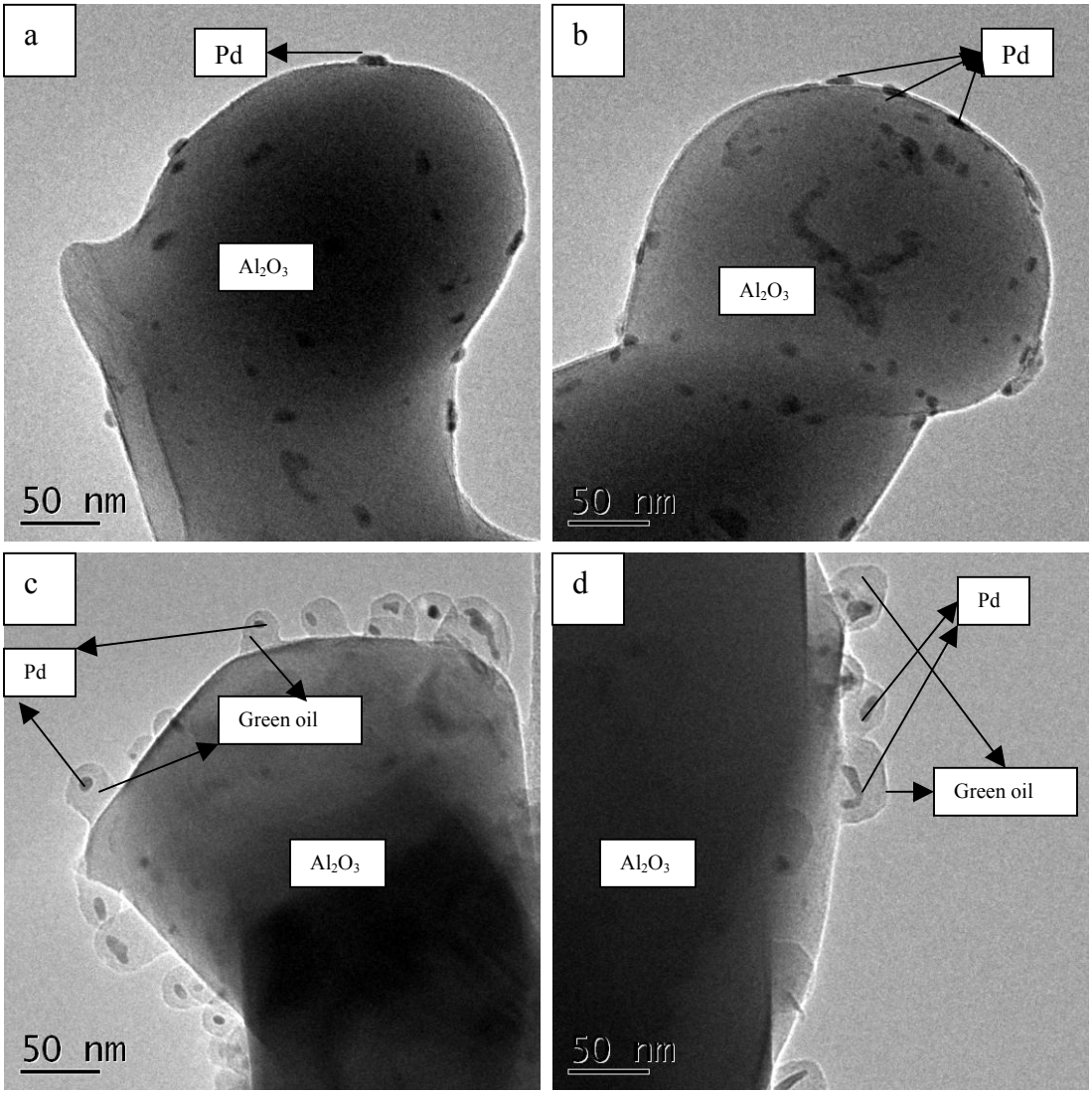

Fig.a-d. 0.1% Pd/Al_2O_3 after 5 hrs at 100°C in various reactant gases. No green oil formed in: (a) C_2H_4 (b) C_2H_4+ H_2; Green oil formed in: (c) C_2H_2 (d) C_2H_2 + H_2.

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