

## Platinum-Catalyzed Enantioselective Hydrogenation of $\alpha$ -Ketoesters: An Unprecedented Surface Reaction of Methyl Pyruvate

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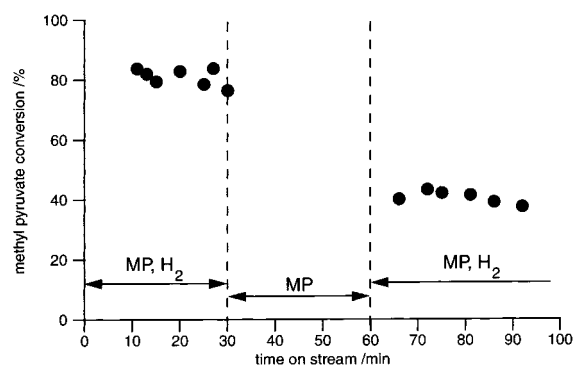
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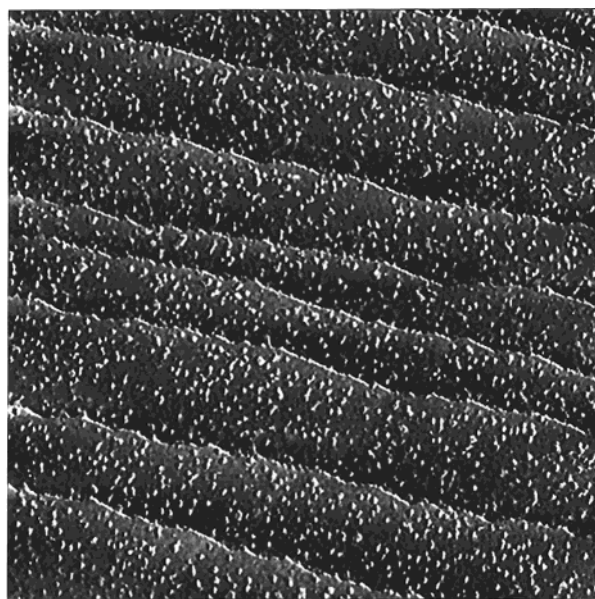
Enantioselective heterogeneous catalysts are rarities although their inherent technical importance is huge. Under appropriate conditions they afford a high degree of stereochemical control and large rate enhancement effects. Indeed, chiral heterogeneous catalysis is a subject of indisputable importance in current chemical research. Such reactions constitute a relatively unexplored field whose theoretical and practical implications are potentially far reaching. Although the number of known systems is growing, the subject as a whole remains, nevertheless, at a relatively early stage of development as is evident from recent reviews.<sup>1,2</sup> This is especially true in regard to fundamental studies of the surface phenomena involved, even in the case of the most studied reactions, including the one which is the subject of this communication—the asymmetric hydrogenation of  $\alpha$ -ketoesters on chirally modified Pt surfaces.<sup>3–5</sup> Although considerable effort has been expended in the past decade to gain a detailed insight into the functioning of this system, there are still a number of key issues requiring clarification. Among these is the question of why the behavior of this catalytic system depends on the sequence of introduction of the reactants (methyl pyruvate, hydrogen) and modifier, as demonstrated earlier by transient kinetic measurements.<sup>6</sup>

We have employed a combination of complementary methods involving solution phase kinetic measurements on a practical dispersed catalyst and studies on a Pt{111} single-crystal surface by means of STM and NEXAFS. We show that in the absence of the cinchona modifier and under conditions of hydrogen starvation the catalyst deactivates due to blocking of the platinum surface by self-condensation of the methyl pyruvate reactant.

Catalytic studies were performed using a 4 mm inner diameter stainless steel tubular fixed-bed reactor system. Details of the reactor, analysis system, and experimental technique are given elsewhere.<sup>7</sup> The catalyst (5 wt % Pt/Al<sub>2</sub>O<sub>3</sub>, Engelhard 4759) was pretreated before use in a separate reactor by flushing with 12 mL·min<sup>-1</sup> N<sub>2</sub> (99.995%) at 673 K for 30 min, followed by a reductive treatment in H<sub>2</sub> (99.999%) for 90 min at the same temperature. After being cooled to room temperature in H<sub>2</sub>, the catalyst was immediately transferred to the reactor and held under nitrogen. Catalyst (500 mg) was applied, resulting in a bed length of 30 mm. Methyl pyruvate (MP, Fluka, 97%) was used without further purification. The reactor was operated at room temperature



**Figure 1.** Fixed-bed reactor transient kinetic experiment of platinum-catalyzed hydrogenation of methyl pyruvate (MP). Feed conditions during different periods of time on stream are indicated. Conditions: Pt/Al<sub>2</sub>O<sub>3</sub> catalyst 500 mg; hydrogen pressure 50 bar; flow rates, hydrogen 5.2 mL·min<sup>-1</sup>, methyl pyruvate 0.5 mL·min<sup>-1</sup>; room temperature.



**Figure 2.** STM image (raw data) of methyl pyruvate on Pt{111} at 298 K in the presence of a background pressure of  $2 \times 10^{-5}$  mbar hydrogen [constant current mode,  $1000 \text{ \AA} \times 1000 \text{ \AA}$ ,  $U_{\text{gap}} = -1 \text{ V}$ ,  $I_{\text{T}} = 10 \text{ nA}$ ].

and a H<sub>2</sub> pressure of 50 bar. STM experiments were carried out using an Omicron UHV STM-1 instrument operating under ultrahigh vacuum conditions (base pressure  $5 \times 10^{-11}$  mbar). This apparatus incorporated LEED and Auger spectroscopy facilities used for surface characterization<sup>8</sup> prior to adsorption experiments. Images were acquired in constant current mode and control experiments indicated that there were no tip-induced artifacts: neither molecular displacements, nor adsorbate decomposition.

The reaction was started by pre-flushing the reactor with hydrogen (5.2 mL·min<sup>-1</sup>) for 5 min and then adding methyl pyruvate (0.5 mL·min<sup>-1</sup>). After 30 min the hydrogen flow was stopped and the reactor was flushed with pure methyl pyruvate for 30 min. After this sequence the reaction was started again by adding H<sub>2</sub> (5.2 mL·min<sup>-1</sup>) for 30 min. Figure 1 illustrates the effect of exposing the catalyst to methyl pyruvate in the absence of H<sub>2</sub>. It is apparent that catalytic activity was strongly suppressed as a result of the hydrogen starvation step. Conversion of pyruvate to methyl lactate fell from 80% to ~40%. The cause of this

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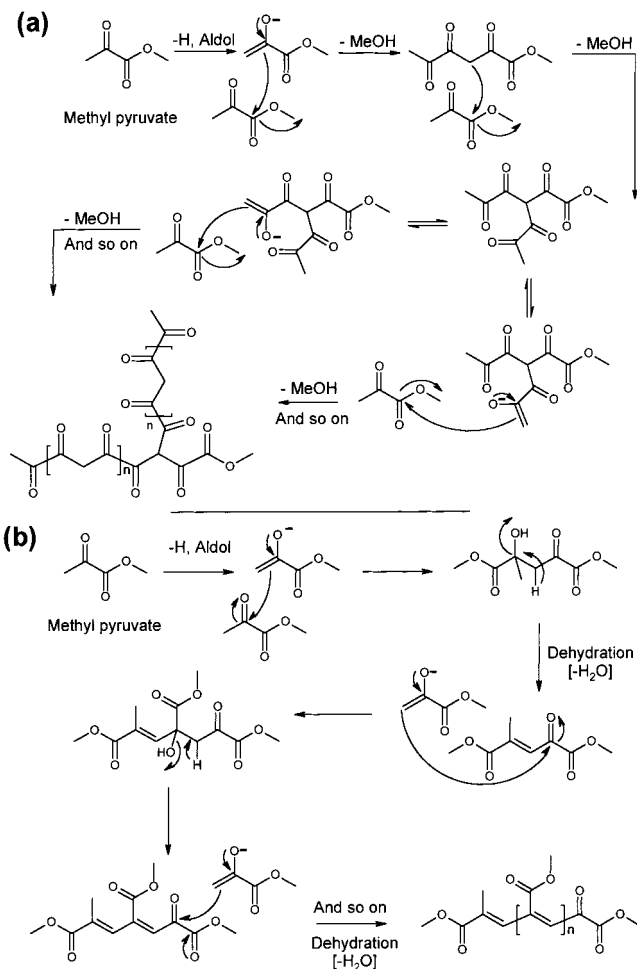
**Figure 3.** Composite STM image (raw data and enhanced edge contrast) of methyl pyruvate on Pt{111} at 298 K in the absence of hydrogen showing the formation of polymeric chains [constant current mode,  $1000 \text{ \AA} \times 1000 \text{ \AA}$ ,  $U_{\text{gap}} = -1 \text{ V}$ ,  $I_T = 10 \text{ nA}$ ].

deactivation was studied by STM, which yields the key information; reference is also made to supporting NEXAFS<sup>9</sup> and XANES<sup>10</sup> data, analyzed and presented in detail elsewhere.

STM images were also taken at room temperature, in the presence and absence of coadsorbed hydrogen. The former were acquired by first dosing the clean surface with hydrogen, then pyruvate, and finally imaging in a standing pressure of  $2 \times 10^{-5}$  mbar of  $\text{H}_2$ . This procedure ensured that all “non-pyruvate” Pt sites were always saturated with H adatoms. Figure 2 clearly shows that, in the presence of  $\text{H}_a$ , methyl pyruvate monomers are distributed uniformly on the terraces of the Pt{111} surface. Identification of these species as monomers is provided by the measured molecular dimensions ( $8 \pm 1 \text{ \AA} \times 3 \pm 0.5 \text{ \AA}$ ) which accord well with the van der Waals dimensions of methyl pyruvate. Thus, the organic reactant has retained its integrity and the whole of the metal surface should be available for catalytic turnover. No long-range order is apparent (consistent with the diffuse  $(1 \times 1)$  LEED pattern) and there is a tendency for the molecules to accumulate at step edges. In the absence of coadsorbed hydrogen the picture is dramatically different, as depicted in Figure 3 (in the upper half of the figure the edge contrast has been enhanced). The monomers have undergone reaction yielding polymeric structures, some of which exhibit dendritic features. These polymeric species are up to  $\sim 320 \text{ \AA}$  long ( $\sim 40$  monomer units) and are uniformly distributed over the Pt{111} terraces. No step decoration is apparent. On such a surface, only about half the initially available Pt sites would be available for catalytic turnover, which happens to be commensurate with our reactor data.

The polymerization of aldehydes and ketones on platinum group metal surfaces is not unknown.<sup>11,12</sup> How might it occur in the case of methyl pyruvate on platinum? Two plausible mechanisms for this process are shown in Figure 4 (a and b). Both are essentially aldol condensations. Mechanism (a) proceeds by elimination of hydrogen and methoxy ( $=\text{MeOH}$ ), mechanism (b) via elimination of water. Both methanol and water are in fact detected in the temperature-programmed reaction (TPR) of pyruvate decomposition on Pt{111}.<sup>9</sup> However, mechanism (b) results in the formation of  $\text{C}=\text{C}$  bonds in the polymeric chains while our NEXAFS spectra of the polymer clearly show that such bonds are not present.<sup>9</sup> We therefore discount mechanism (b).

Mechanism (a) involves initial attack at the ester carbonyl (the most electron deficient center). Once the first “dimer” is produced,



**Figure 4.** Possible mechanisms for methyl pyruvate polymerization on platinum.

the most acidic proton lies in the middle of the resulting molecule: this provides the possibility of subsequent chain growth taking place either linearly or in a branching fashion, in accord with Figure 3. Furthermore, the resulting polymeric structures containing only the  $\text{C}=\text{O}$  function are in excellent agreement with our NEXAFS<sup>9</sup> and XANES data.<sup>10</sup>

We conclude that, under certain conditions, self-condensation of the  $\alpha$ -ketoester can be an important side reaction in the enantioselective hydrogenation of methyl pyruvate on Pt surfaces. This occurs in the absence of the cinchona modifier when the ratio of  $\text{H}_a$  to adsorbed  $\alpha$ -ketoester is too low. Our findings emphasize the great importance of employing correctly chosen start-up conditions and careful control of reactant concentrations during catalyst operation, so as to avoid hydrogen starvation. Catalyst deactivation due to self-condensation of the reactant as shown here for methyl pyruvate hydrogenation is also likely to occur with other  $\alpha$ -ketoesters employed in this reaction.

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