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DIRECT DETERMINATION OF BLOCKING OF SURFACE DEFECTS
BY CARBONACEOUS DEPOSITS DURING HYDROCARBON REACTIONS
ON PLATINUM SINGLE CRYSTALS

by

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Many catalytic reactions are believed to occur at specific surface sites with well defined geometries. This explanation is frequently invoked to explain changes in catalytic activity as a function of particle size on supported catalysts. The influence of metal particle size on the catalyst activity for hydrocarbon conversion was first reported by Gault [1], and it is a topic that has attracted extensive research since [2,3]. The results of such studies are sometimes contradictory, but it is generally accepted that many reactions are sensitive to the catalyst topography at the molecular level. Noticeable changes in either reaction rates or product selectivity have been reported for conversion of molecules like butane [4] and neopentane [5,6]. Similar changes have been seen by Anderson [7] and by Santacessaria [8] for n-hexane reactions over ultra-thin films and over platinum particles smaller than 10 Å supported on silica. Dautzenberg and Platteuw [9,10] and Ponc and coworkers [11], on the other hand, did not find any significant structure sensitivity for the same system using catalysts with particle size from 15 to 80Å in diameter.

The structure sensitivity of these reactions can be explained by the combined effects of two or three structural features. Firstly, the surface of metal particles are composed of a combination of faces with different crystallographic orientations, including close packed planes ((100) and (111) planes for fcc metals). There are also edges, corners, and other irregularities on the surface that may display different catalytic behavior than the flat terraces. The ratio of metal atoms on terraces to those at

defects changes dramatically with particle size. A third contribution, due to the metal-support interface, has been invoked to explain some of the experimental results [17].

In order to understand the importance of these different sites to the overall performance of the catalyst in more detail, we have recently studied the catalytic conversion of several hydrocarbons over a series of single crystal surfaces with selected orientation [12,13,14]. It was found that isomerization and consecutive rearrangement of light alkanes (isobutane, n-butane, and neopentane) were maximized on platinum surface with high concentration of (100) microfacets [12]. Reactions over stepped and kinked surfaces also show enhanced activity over flat metal surfaces. n-Hexane isomerization by contrast was structure insensitive [13]. Only n-hexane aromatization was accelerated by the presence of (111) terraces.

In this note, we report determination of the relative importance of terraces, steps and kinks for catalyzing hydrocarbon conversion reactions using n-hexane, methylcyclopentane, isobutane and neo-pentane. The high pressure - UHV apparatus used in these studies is described in detail elsewhere (5). It is equipped with standard surface science instrumentation (Auger electron spectroscopy, mass spectroscopy, low energy electron diffraction), and a retractable cell to isolate the sample from vacuum and enclose it in a loop that acts as a well mixed batch reactor for high pressure reactions. Four platinum single crystals were employed, cut in the (111), (557), (332), and (10,8,7,) orientations. A schematic representation of these surfaces is shown in fig. 1. They all have (111) terraces but different kinds of steps and kinks.

Initial rates for isobutane, neopentane, n-hexane and methylcyclopentane (MCP) conversion are presented in fig. 2 for the four platinum crystallographic faces. n-hexane and MCP activities vary only slightly in the presence of the different irregularities. Isobutane and neopentane, on the other hand, react as much as four times faster when defects are present on the catalyst surface. A more detailed discussion of the results obtained for the lighter alkanes have been presented elsewhere (12, 13).

Only a small fraction of the surface area of the metal is actually active for catalysis. More than 50% of such surfaces are covered by carbonaceous deposits during actual catalytic condition [16]. These residues passivate the metal and inhibit further hydrocarbon conversion. Carbon monoxide adsorption - thermal desorption methods were developed to titrate active platinum sites before and after reaction rate studies [16]. This technique provides information not only on the amount of uncovered surface available for catalysis, but also on the nature of these sites. Examples of results obtained from these studies are shown in fig. 3. The topmost trace represents a standard thermal desorption spectrum obtained after co-saturation of a (775) stepped platinum surface (also called Pt(s) - 6(111)x(100)). The major peak at 430K is due to desorption from the (111) terraces, while the high temperature shoulder originates from desorption from the steps. The two distinctive adsorption states allow us to monitor the structural changes that occur as a result of the carbon deposition during hydrocarbon reactions. Fig. 3 also shows that after isobutane and neopentane reactions, a fraction of both terrace and step platinum atoms are still uncovered by carbon, roughly in proportion to their concentration ratio on the clean platinum surface. After reactions with n-hexane and methylcyclopentane, on the other hand, only a

fraction of the terraces remain catalitically active as the high temperature CO desorption peak, due to desorption from the steps, disappears indicating the passivation of step sites by deposited carbon.

There is a good correspondence between changes in reaction rates and selectivity of site blocking for these hydrocarbon conversion processes. Isobutane and neopentane isomerization and hydrogenolysis proved to be faster over surface with steps and kinks. The increase in reactivity can be associated with the atoms at defect sites because they are not covered by hydrocarbon residue and are therefore available for catalysis. Methylcyclopentane and n-hexane reaction rates were similar for the four crystals studied here. This result is to be expected because steps and kinks become covered by organic fragments and therefore deactivated by carbonaceous residues within the first minutes of reaction, the catalysis occur only on (111) terraces on all surfaces.

Our experiments have been carried out under highly reducing conditions, with hydrogen to hydrocarbon ratios between 10:1 and 30:1. Since these ratios are higher than those used in commercial processes, we expect that our results are applicable to supported catalysts.

In conclusion, a CO titration techniques was developed to directly identify catalytic sites on platinum single crystal surfaces. The importance of irregularities on the metal surface for isobutane and neopentane conversion was established using this method. N-hexane and methylcyclopentane reactions, on the other hand, are not affected by the presence of such defects as these heavier alkanes deposit carbonaceous fragments at the surface irregularities that passivates them during both catalytic reactions and for CO adsorption.

As a result structure sensitivity that is due to defects at the surface (steps and kinks) should be absent for the reactions of heavier alkanes while very much present for lighter alkanes.

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FIGURE CAPTIONS

- Fig. 1. Idealized atomic surface structures for the flat (111), stepped (332) and (755), and kinked (10,8,7) platinum single crystal surfaces.
- Fig. 2. Structure sensitivities for alkane conversion catalyzed over platinum single crystal surfaces.
- Fig. 3. Comparison between CO thermal desorption from (755) platinum surface clean and following hydrocarbon reactions. CO adsorption temperature = 310-315K. Heating rate = 80K/s. CO exposure = 36L.

Fig. 1.

XBL 819-2032D

Fig. 2.

XBL 846-7091

CO thermal desorption
following reaction studies
on Pt(S) - [6(111) × (100)]

Fig. 3.

XBL 816-974 A

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