Microwave Effects in Catalysis

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Many attempts have been made to employ energy as a selective co-reagent in catalytic reactions. Photocatalysis employs visible light for a variety of oxidation reactions on a very limited series of catalysts, e,g, employing TiO_2. In contrast, attempts to excite specific atom-atom bonds of adsorbed species in the infrared by vibrational resonance have not proved to break the specific bonds selectively. The differences are significant. Many recent studies have suggested that microwave energy can be employed in catalysis and that the results differ from "conventional" heating of the systems studied. Although "photocatalysis" is well accepted, "microwave-catalysis" has not here-to-fore been accepted as an approach to change the selectivity or efficiency of catalysis in the presence of microwave energy. We have studied the influence of microwave energy on sorption and catalysis, particularly on selective desorption, automotive exhaust catalysis and the synthesis of zeolites. Our initial experiments have demonstrated that microwave energy can selectively heat a system such that the gaseous temperature can be lower than the solid temperature that is lower than the unmeasured surface temperature. The fundamental question is "What is the surface temperature during adsorption under exposure to microwave radiation?"
The development of a new generation of automotive exhaust catalysts faces several significant challenges, which might be overcome by the use of microwave energy. The first is to increase the activity in removing pollutants (e.g., CO and unburned hydrocarbons) as soon as possible. A disproportionate fraction of the pollutants are produced as the catalyst is heated up to operating temperature, as it "lights off." The second challenge are the influences of sulfur contaminants which impede the catalytic activity, particularly during light off. We find that indeed microwave energy can induce catalyst light off for CO oxidation more efficiently than conventional heating and can reverse the poisoning by SO_2 for a commercial three-way catalyst. However, NO reduction is inhibited in the presence of microwave energy.

We have shown that microwave energy can be absorbed selectively on the surface of oxide supported catalysts(1). The result is a rapid, efficient, selective heating of the surface. As a consequence, desorption can be induced without the necessity of heating the whole system to the same temperature. Potentially, catalytic reactions at the surface can be induced by less energy while the bulk is still at a lower temperature, such as during light off. Numerous studies have demonstrated that the sulfur present in gasoline decreases the effectiveness of catalyst for the control of contaminants (hydrocarbons, CO and NOX) in auto exhaust (1-4). The current "state-of -the-art" solution to the control of vehicle emission will need to be modified or replaced to meet the future requirements. It is generally believed that oxides of sulfur are the dominant forms of sulfur present in auto exhaust. These will adsorb on the catalyst surface to form sulfates and sulfides by reaction with surface species. Sulfur is perceived to react with the noble metals to form sulfides and with the ceria to form sulfates. Ideally, microwave energy alone might decompose the sulfides and sulfates on the surface.

These are the most polar and polarizable bonds in the whole system and would be most receptive to absorb microwave energy.

Three experimental studies will be discussed.
a) We studied the influence of microwave energy on selective sorption. Mixtures of gaseous species are passed over a catalyst/sorbent with and without exposure to microwave energy. The effluent changes with exposure to microwaves, changing the sorption selectivity.
b) We studied the influence of microwave energy on a commercial, state-of-the-art, three-way catalyst (Englehard Corp.) with simulated exhaust feeds. Continuous microwave energy at different power levels and 2.45 GHz was employed in a flow system with a mass spectrometer to monitor the effluent.
c) We studied the influence of microwave energy on the equilibrium for adsorption of differing species compared to their adsorption isotherms without microwave exposure.

We conclude that microwave energy is selectively adsorbed by the surface/adsorbed-layer of the three-way catalyst. The catalyst lights off at lower temperatures that if the whole catalyst were heated by conventional means. The “effective” temperature is very local and the rate of heat transfer is not as fast as desorption/reaction. CO oxidation is enhanced due to the heating while NO reduction is inhibited due to selective desorption. Thus, the “effective “ surface temperature is higher than the support or gas-phase temperatures. We cannot measure the local “effective” temperature directly. We employ adsorption isotherms to infer the "effective surface" temperature with exposure to microwave radiation. This temperature can be significantly higher than the gas or solid and depends on the adsorbate. Increasing the adsorbate pressure can even decrease the amount adsorbed as the "effective" surface temperature increases. The implications of these results to separations and catalysis will be discussed. These studies give considerable insight into the potential influence of microwave energy on heterogeneous catalytic reactions, a “microwave effect”. Specifically, the influence will be greatest if the energy can be directed to the surface, i.e., the bulk is transparent to microwave energy. The concentration of energy due to microwave energy on the surface will depend on the nature of the surface (hydroxyls, etc.), active sites (metals), and the specific adsorbing (reacting or desorbing) species. It is also important that the reaction, or desorption, can occur prior to thermal equilibration; otherwise, there will be little difference for microwave induced sorption/reaction compared to conventional heating.

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