PULSED MICROWAVE CATALYTIC DECOMPOSITION OF OLEFINs

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ABSTRACT

The application of the recently developed, versatile and economic technique of microwave assisted catalysis to the reactions of olefinic hydrocarbons, principally ethylene, propylene and 1-pentene is discussed. The reactions are believed to involve free radical intermediates and can result in efficient conversions to selected aliphatic and aromatic hydrocarbons.

INTRODUCTION

Recent years have witnessed an exponential expansion in the variety of applications of microwave energy to chemical processes and chemical reactions. In this laboratory we have spent the last decade exploring the unique attributes of the selectivity of microwave interactions with materials of different types as a basis for initiating and controlling chemical reactions over various catalytic surfaces. Although low frequency microwave radiation is not itself energetic enough to initiate chemical reactions in organic compounds we have developed the concept of using materials which strongly absorb microwave radiation as "sensitizers" to focus and efficiently transfer the microwave energy to the desired chemical substrates. The efficacy of this technique has been successfully demonstrated in a variety of systems including the water gas shift reaction [1], the hydrodesulfurization of hydrocracked pitch [2], and the oxidation of
hydrocarbons to alcohols, aldehydes, and acidic products using water as the oxidizing reagent [3,4,5]. The conversion of methane to higher hydrocarbons has been used as a model system for more detailed studies of the effects of changing the microwave pulse train characteristics as well as other experimental parameters on the product yields and distribution [6,7]. More recently the technology has been successfully applied to problems of environmental significance including the decomposition of acid gas air pollutants including SO2 and NOx [3], and the dehalogenation of both aliphatic and aromatic halohydrocarbons [4,8,9]. Both hydrogenation and dehydrogenation of cyclohexene can be effected by this technique [10].

In this report we wish to discuss the reactions of olefins such as ethylene, propylene and 1-pentene, initiated by pulsed microwave irradiation, over metal catalyst surfaces. Ethylene and propylene are feedstocks of primary importance in the polymer and petrochemical industries. We can show that these olefins can be rapidly, efficiently and cleanly converted to other hydrocarbon products. The microwave assisted catalytic technology has a principal attribute of flexibility; relatively minor changes in experimental conditions can tailor the product distributions to favour either C1-C2 products which are believed to be the primary products in the reactions, or to favour C6 or higher hydrocarbons including aromatics which are secondary reaction products. Such easily modified reaction conditions include changes in the catalyst nature, the carrier gas pressures and composition, and the microwave pulse characteristics. These latter include peak power, duration and period - in these experiments the commercial microwave frequency of 2.45 GHz is used.

In previous studies the microwave activated catalysis has been shown to require a source of moderately high power microwave energy which can be pulsed in a controlled manner, and a catalyst surface which ideally contains both material which efficiently absorbs microwave radiation and which adsorbs the reagents of interest. Then repetitive, short pulses of microwave radiation rapidly "heat" the catalyst surface sufficiently for chemical reactions to be initiated; pauses between radiation periods allow control of the surface temperature and time for the products to desorb. The bulk of the reagent medium and indeed the catalyst support if it is non-absorbing remain close to ambient temperature. It is this concentration of the microwave energy at the reaction sites which enhances the efficiency of the process; it also minimizes unwanted side or back reactions in the bulk of the reagent volume. This efficiency and flexibility of the microwave assisted technology is expected to be a primary impetus for its expansion to future applications.