

Microwave-Activated Oxidative Dehydrogenation of Ethane over Oxide Catalysts.

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Introduction

Microwave (MW) irradiation is among the most promising and attractive methods for catalyst activation due to following distinctive features: (1) the MW treatment provides a tool for non-equilibrium changes in catalyst structure, which cannot be achieved by conventional thermal and chemical treatments, neither in *ex situ* (during catalyst preparation), nor in *in situ* (in the course of catalytic reaction) modes; (2) frequency and intensity variation of the applied field enables a tunable and targeted modification of the solid system.

Positive effect of MW treatment was reported for such catalytic reactions as hydrogenation of chlorinated phenols, isomerization of hydrocarbons, CO oxidation, deNO_x and deSO_x, methane conversion, etc. Most authors explain it by the formation of "hot spots" [1] - areas having higher temperatures compared to their surroundings due to their greater interaction with microwaves and slow heat dissipation. The detection of hot spots in heterogeneous catalysis is difficult because their size can be on a nanometer range. Spatial resolution of commonly used methods for temperature registration is not enough for their detection, and only some averaged temperature of the catalyst can be measured. This is one of the reasons why even a reliable ascertainment of the existence of the difference between conventional (thermal) and MW excitation of the reaction system can be difficult.

In this work a kinetic approach for the comparison of catalytic performance in different modes of excitation (MW vs. thermal) is suggested. It consists in the comparison of apparent kinetic parameters (activation energies), and dependencies (shape of kinetic equations, "selectivity or yield vs. conversion" curves) obtained in two modes. This approach has been applied to the study of oxidative dehydrogenation (ODH) of ethane over a series of complex oxide catalysts.

Catalysts and experimental setup

A series of vanadium-containing mixed oxides (VSb, VMo, VMoNb) was prepared by conventional evaporation-precipitation method and tested as catalysts for ethane ODH at conventional thermal heating (by electric furnace) and under MW irradiation. In the second case, the reactor with a catalyst was placed into the cavity of low-power (≤ 50 W) MW system continuously operated at frequencies ranging from 3.4 to 3.8 GHz. Measuring circuit allows to measure both incident and reflected MW power. The catalyst temperature was varied by tuning the incident MW power and monitored using a MW-transparent optical fiber sensor.

Two series of experiments in each mode were carried out: gas flow rate variation at constant temperature (450°C) and temperature variation at constant flow rate. Reaction mixture was analyzed by conventional on-line GC.

Results and Discussion

Preliminary heating test showed that the catalysts under study can be heated in air easily in a MW mode to typical ethane ODH temperatures (400-500°C). The most promising results were obtained while heating the VMoNb-oxide catalyst. During heating in air it has changed its color from green to orange. This is an evidence for a deep oxidation of constituent cations (in particular, vanadium transformation to V⁵⁺ state), what cannot be reached by regular thermal oxidation in air. Even after treatment in the reaction mixture (C₂H₆ : O₂ : N₂ = 2 : 1 : 3) in a MW mode this sample retained spots of orange color on the external surface of the grains.

The analysis of reaction kinetics demonstrated that in both modes of operation the overall rate can be satisfactorily described by a simple first-order equation. However, as can be seen from Figure 1, whereas for VSb oxide no difference in "ethane yield vs. conversion" curves obtained in two modes is observed, in the case of VMoNb oxide a distinct difference between ethane yields is observed at given conversion of limiting reactant (oxygen). Since for the same VMoNb-catalyst no significant difference in Arrhenius plots in two modes is noted (see Figure 2), one may suggest that the unusual structures existing in the conditions of MW irradiation contribute to the reaction on the stage of consecutive transformation of intermediate products. By contrast, in the case of VMo-oxide two Arrhenius plots differ significantly. This is an indication of the participation of MW-generated structures in activation of reactant molecules.

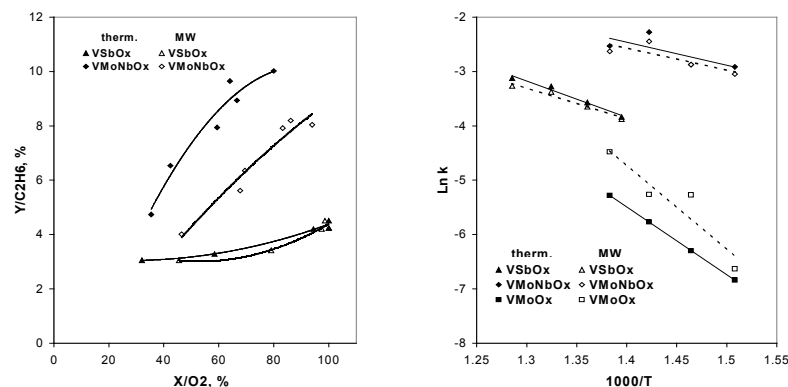


Figure 1. Yield of ethylene as a function of oxygen conversion at 450°C.

Figure 2. Arrhenius plots for 1-st order ethane conversion rate constants.

Significance

The new approach for the analysis of the effect of MW treatment on catalytic performance is suggested and applied for the studies of industrially important reaction – ethane ODH to ethylene.

References

1. X. Zhang, D.O. Hayard, D.M.P. Mingos, *Chemm. Commun.* 975, 1999