On the Possible Causes of Enhancement of the Heterogeneous Catalytic Liquid-Phase Oxidation Reaction of *m*-Xylene by Microwave Radiation

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Abstract—The contribution of the heterogeneous component of the total conversion of m-xylene to the process of its heterogeneous catalytic liquid-phase oxidation has been studied, as this contribution is most clearly manifested in the case of microwave treatment. It has been shown that microwave irradiation shortens the induction period of the reaction taken to reach a steady state. It has been suggested that the observed increase in the generation rate of free m-xylyl radicals by microwave treatment is due to the appearance at the hydrocarbons/catalyst interface of local overheating regions whose temperature can exceed the weight-average temperature in the reaction space.

Keywords: heterogeneous catalysis, microwave radiation, *m*-xylene, oxidation, radical chain process, heterogeneous component of total *m*-xylene conversion

DOI: 10.1134/S0965544113020047

Coming in line with the latest new challenges of development of power-savings processes for heavy organic and petrochemical syntheses is microwave chemistry, including microwave chemistry of heterogeneous catalysis, which deals with a variety of heterogeneous catalytic transformations of substances induced by a microwave (MW) electromagnetic field [1-4].

In contrast to the traditional conditions of thermal treatment of the reaction medium-catalyst system, feedstock during a process in an MW field has a lower temperature, since the main component of the reaction system that absorbs radiation and converts MW energy into heat is the heterogeneous catalyst per se. In this case, the specifics of microwave treatment will be most prominently manifested in heterogeneous catalytic liquid-phase processes of hydrocarbon conversion, in which local temperature above the weightaverage temperature of the reaction system at the solid/liquid interface can be achieved owing to both the difference of dielectric losses and a relatively low thermal conductivity of the reaction medium. This could lead to prevalence of heterogeneous catalytic routes of *m*-xylene transformation, such as the generation of *m*-xylyl radicals and degradation of *m*-methylbenzyl hydroperoxide, over the identical homogeneous routes and, consequently, to a change in the ratio of the principal to the side product formation rates.

Previously [5, 6], we investigated the activity of $Co-Mn/Al_2O_3/Al$ framework catalysts in the liquidphase oxidation of *m*-xylene to *m*-toluic acid, which follows the radical chain heterogeneous-homogeneous mechanism. It was shown that in comparison with the initiated oxidation of *m*-xylene and its conversion in the presence of monolithic Co-Mn samples, higher values of the ratio of the heterogeneous surface area to the volume of the liquid phase (*S/V*) characteristic of supported catalysts can lead to higher initiation and propagation rates during both the initiation and the reaction propagation periods.

In [7], it was also found that microwave irradiation of the *m*-xylene–Co–Mn/Al₂O₃/Al reaction system of an identical composition noticeably shortens the reaction time to achieve the maximum yield of the desired product *m*-toluic acid as compared with conventional reactor heating with an electric heater.

In this study, we attempted to reveal possible causes of the enhancement of the aforementioned reaction assisted by microwave electromagnetic radiation.

EXPERIMENTAL

The experiments were carried out in the setup composed of a reaction unit with an outer gas $(N_2 + O_2)$



Fig. 1. The kinetics of oxygen uptake (a) in the absence of inhibitor, (b) with introduced $(5.5 \times 10^{-4} \text{ mol/L}) N, N'-\text{di-}\beta$ -naphthyl-*n*-phenylenediamine (marked by arrow), and the reciprocal of the oxygen uptake rate in the presence of the Co–Mn/Al₂O₃/Al catalyst. Magnetron power 600 W. Weight-average temperatures, 413 K; the ratio $S/V = 3 \times 10^6 \text{ m}^{-1}$.

circulation loop and constructed on the basis of a Panasonic EM-G5593V microwave oven having a cavity volume of 23 L, a variable radiation generator power of 200–800 W, and an operating frequency of 2450 MHz. The temperature in the reaction zone was monitored using a VA6520 remote noncontact infrared pyrometer with a measurement range of -50 to 600°C. Excess heat was withdrawn from the reaction zone with an effluent stream of the oxygen–nitrogen mixture. To avoid unexpected overheating of the reactor, a ballast container with circulating distilled water was mounted in the oven cavity.

Most components of the liquid phase of the catalyzates were identified by GLC, via matching the retention volumes of the products with those found for the relevant commercial chemicals [5]. The amount of m-methylbenzyl hydroperoxide in the products was determined by iodometric titration of the samples according to the procedure described in [8].

The rate of generation of free radicals, both under microwave irradiation and in the case of conventional heating, was measured as the oxygen uptake rate $(W_{O_2}^{inh})$ in the presence of N, N-di- β -naphthyl-n-phe-nylenediamine (5.5–6.0 × 10⁻⁴ mol/L) as the inhibitor introduced into the system during the reaction and was calculated by the formula:

$$W_{inh} = \frac{2\Delta[\text{In}H]}{S \cdot \tau_{inh}},\tag{1}$$

where W_{inh} is the inhibitor consumption rate (mol/(m² min)), Δ [In*H*] is the amount of the inhibitor

consumed (mol), *S* is the surface area of a catalyst sample (m²), 2 is the stoichiometric coefficient of inhibition, and τ_{inh} is the length of time (min) cut on the abscissa by extrapolating the curve in the $1/W_{O_2}^{inh} - \tau$ coordinates (Fig. 1).

As the origin of a new time coordinate, the inhibitor introduction time (indicated by the dashed arrow) was taken. The consumption of the inhibitor was monitored by following the buildup of its colored oxidation product N,N-di- β -naphthyl-p-quinonediimine, whose concentration in the catalyzate samples was determined on an SF-4A spectrophotometer by measuring absorption at a wavelength of $\lambda_{max} = 480$ nm with the molar absorption coefficient of $\varepsilon = 1.1 \times 10^4$ L/(mol cm).

RESULTS AND DISCUSSION

It was found that the introduction of the inhibitor at the onset of the reaction does not result in complete inhibition of oxygen absorption; however, this is not due to the ineffectiveness of the inhibitor, rather, it is associated with the presence of uninhibited heterogeneous catalytic routes of *m*-xylene transformation.

Assuming that the free radical generation process under the conditions of underdeveloped propagation of the chain reaction is controlled by the step of heterogeneous catalytic initiation, we can estimate its rate as the difference of the oxygen uptake rate in the presence of the inhibitor ($W_{O_2}^{inh}$) and the chain inhibition rate (W_{inh}):

$$W_{R} = W_{O_{\gamma}}^{inh} - W_{inh}.$$
 (2)

Figures 2 and 3 show the dependence of the initial rate of heterogeneous catalytic initiation for the chain oxidation of *m*-xylene at its conversion of no more than 8-10% when the effect of change in the hydrocarbon concentration on the kinetics of the radical chain process can be ignored.

It is seen that for fixed values of the steady-state weight-average temperature in the reactor, identical amounts of the catalyst, and the same oxygen concentrations, the initial rate of heterogeneous catalytic generation of free radicals (W_R) under microwave irradiation is greater than that under the conventional heating conditions. In this case, as the reaction temperature achieved by increasing the magnetron power rises, the difference in the generation rates of free radicals becomes more apparent (Fig. 4).

The observed proportionality of W_R to the oxygen concentration and the amount of catalyst introduced can be explained in terms of the following scheme of the formation of free radicals via the interaction of *m*xylene with the active sites on the heterogeneous catalyst surface (phase 2 is expected to be slow):

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Fig. 2. Dependence of the initial rate of heterogeneous catalytic chain initiation on the surface of the Co–Mn/Al₂O₃/Al catalyst upon the oxygen concentration at $S/V = 3 \times 10^6$ m⁻¹ and the amount of the catalyst at $C_{O_2} = 6.5 \times 10^{-4}$ mol/L in the modes of (1, 3) conventional heating and (2, 4) microwave heating at a microwave power of 600 W. The weight-average temperature is 403 ± 2 K.

$$RH + Z_{(\text{oxid})} \xrightarrow{k_1} R \bullet + Z_{(\text{red})}$$

$$Z_{(\text{red})} + O_2 \xrightarrow{k_2, slow} Z_{(\text{oxid})} + H_2O,$$
(3)

where $Z_{(oxid)}$ is an oxidized site and $Z_{(red)}$ is a reduced site on the catalyst surface.

According to this scheme, the rate of generation of free radicals on the heterogeneous surface in its quasisteady state can be equated to the formation rate of reoxidation sites Z_{oxid} :

$$W_{R\bullet} = \frac{d\mathbf{R}\bullet}{d\tau} = k_1[\mathbf{R}\mathbf{H}]\Theta_{(\text{oxid})} = \frac{dZ_{(\text{oxid})}}{d\tau}$$
(4)
= $k_2\Theta_{(\text{red})}[\mathbf{O}_2] - k_1[\mathbf{R}\mathbf{H}]\Theta_{(\text{oxid})},$

where [RH] is the initial concentration of *m*-xylene (mol/L); [O₂] is the concentration of dissolved oxygen (10⁻³ mol/L); k_1 and k_2 are the rate constants of reduction and reoxidation of active sites, respectively; and $\Theta_{\text{(oxid)}}$ and $\Theta_{\text{(red)}}$ are respectively the normalized-tounity concentrations of oxidized and reduced sites on the catalyst surface:

$$\Theta_{\text{(oxid)}} + \Theta_{\text{(red)}} = 1.$$
 (5)

Solving Eq. (4) with respect to Θ_{oxid} using simple transformations, we obtain the following expression

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Fig. 3. Dependence of the initial rate of heterogeneous catalytic chain initiation on the surface of the Co–Mn/Al₂O₃/Al catalyst upon the oxygen concentration at $S/V = 3 \times 10^6$ m⁻¹ and the amount of the catalyst at $C_{O_2} = 6.5 \times 10^{-4}$ mol/L in the modes of (1, 3) conventional heating and (2, 4) microwave heating at a microwave power of 450 W. The weight-average temperature is 403 ± 2 K.

for the specific free-radical initiation rate normalized to the unit area of the catalyst loaded:

$$W_{R} = \frac{d\mathbf{R} \bullet}{d\tau} = \frac{k_1 [\mathbf{R}\mathbf{H}] k_2 [\mathbf{O}_2]}{k_1 [\mathbf{R}\mathbf{H}] + k_2 [\mathbf{O}_2]}.$$
 (6)

Under the experimental conditions when $k_1[RH] \ge k_2[O_2]$, we get:

$$W_{R\cdot} = \frac{d\mathbf{R} \bullet}{d\tau} = k_2 \left[\mathbf{O}_2 \right] = k_{R\bullet} C_{\mathbf{O}_2} = k_0 e^{-\frac{\mathbf{E}a}{RT}} C_{\mathbf{O}_2}, \qquad (7)$$

where k_{R} – can be considered the specific rate constant of heterogeneous generation of *m*-xylyl radicals, E_a is the activation energy, and k_0 is the pre-exponential factor.

The table lists values for the rate parameters of the step of heterogeneous generation of *m*-xylyl radicals in the case of conventional heating of the reactor and heating by MW irradiation, as calculated from the Arrhenius plot of $k_{R_{\bullet}}$ versus temperature on basis of arrays of experimental data approximated by Eq. (7).

It is seen that the values of the specific rate constants of heterogeneous generation of *m*-xylyl radicals in the case of microwave irradiation of the reaction system exceed those for conventional heating, with the

Parameter	Heating with electric heater				MW irradiation			
Weight-average temperature, K	388	398	403	413	388	398	403	413
$k_{\rm R}$, mol/min	1.15	2.31	3.69	7.23	2.84	5.23	7.15	18.53
E_a , kJ/mol	122.5				121.8			
$\log k_0$	16.3				16.7			

Kinetic parameters of the step of heterogeneous generation of *m*-xylyl radicals in different modes of thermal treatment of the reaction system

difference in the values of the constants sharply increasing with the increasing reaction temperature.

It is noteworthy that the activation energy values for the generation of free radicals in both modes of energy input remain almost unchanged. This invariability suggests the absence of the "nonthermal" effect in the activation of m-xylyl radical generation because of a relatively low microwave quantum energy compared with the C–H bond energy in the xylene molecule [9].

In conclusion, taking into account the above circumstances, we may assume that owing to the differ-



Fig. 4. Dependence of the initial rate of heterogeneous catalytic chain initiation on the surface of the Co-Mn/Al₂O₃/Al the catalyst upon the weight-average temperature at an oxygen concentration of $C_{O_2} = 6.5 \times 10^{-4}$ mol/L and upon the amount of the catalyst at $S/V = 10^{-4}$ mol/L and upon the amount of the catalyst a

 3×10^6 m⁻¹ in the modes of (1) conventional heating and (2) microwave heating at input powers of 200, 320, 480 and 640 W.

ence of dielectric loss in the bulk of the heterogeneous catalyst and in the bulk of m-xylene subjected to oxidation, local overheating spots emerge at the oxidized hydrocarbon/catalyst interface, so that their temperature exceeds the weight-average temperature in the reaction space. This fact, because of a reduction in the value of the exponent in Eq. (7), seems to be the real cause of the observed increase in the specific rate of initiation of free radicals in the microwave-enhanced process of heterogeneous catalytic oxidation of m-xylene and, under the conditions of developed propagation of the time required to reach the maximum yield of m-toluic acid [7].

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