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Benzene hydrogenation in the thiophene presence over the sulfide Ni-Mo/γ-Al_2O_3 catalyst under periodic operation: Kinetics and process modelling

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Abstract

An unsteady-state kinetic model of both benzene hydrogenation (HDA) and thiophene hydrogenolysis (HDS) on the sulfide hydrotreating catalyst Ni-Mo/Al_2O_3 has been developed. The model adequately describes experimental data obtained at the pressure 2 MPa, temperature 573 K and at various contact times and ratios of benzene/thiophene. The model is based on the assumption that the catalyst surface contains only one type of active sites, i.e., Ni atoms in the sulfide bimetallic species, which are responsible for both hydrogenolysis and hydrogenation reactions. On the base of the kinetic model, a theoretical analysis of the reactor performance under unsteady state conditions was carried out. The unsteady state conditions on the catalyst surface are supposed to be created by forced oscillations of thiophene concentration in the reactor inlet (periodic operation of reactor). The influence of various parameters like cycle split, length of period of forced oscillations in the reactor was investigated with respect to the conversion of the benzene. It is shown that for periodic reactor operation an average conversion was up to several times higher than a steady state value.

Keywords: Transient kinetics; Sulfide catalyst; Benzene hydrogenation; Periodic operation

1. Introduction

One of the important subjects of environmental catalysis is research on clean fuels [1,2]. In the past decade, some areas of the research on clean fuels included hydrodearomatization (HDA) and hydrodesulfurization (HDS), which proceed on sulfide (Ni, Mo) and (Ni, W) catalysts. Currently, the fuel specifications for all highway diesel fuels in the US, Japan, and western Europe limit the sulfur content of the diesel fuels to be less than 0.05 wt.% or 500 parts per million by weight (ppmw). The new Environmental Protection Agency (EPA) regulations reduce the sulfur content of the highway diesel fuel from 500 ppmw (1989) up to 15 ppmw (June 2006). In this case, the volume of catalyst bed will have to be increased 3.2 times as that of the current HDS catalyst bed. If reducing the sulfur level to 0.1 ppm the volume of catalyst bed will have to be increased by about seven times [2]. Therefore, new catalysts and processes of fuels treatment are necessary. Furthermore, environmental problems stimulate novel investigations in this field of catalysis. As it is well known, a difficult problem of the HAD–HDS processes on sulfide catalysts is the mutual inhibition of hydrogenation reactions by sulfur–organic compounds and of hydrogenolysis reactions by aromatics.

At the same time, experimental and theoretical studies in heterogeneous catalysis during the last decades have given evidence that reactor performance under unsteady state conditions can lead to improved process efficiency compared to steady state operation. Under transient conditions, it is possible to maintain the catalyst surface in an optimal state increasing the average reaction rate and selectivity towards a specific product resulting in an enhanced reactor performance. One of the ways to attain the catalyst unsteady state is forced oscillations of the reactant concentrations (periodic reactor operations) [3–5]. To model these transient regimes of reactor operation of HAD–HDS processes it is necessary to have unsteady state kinetic model taking into account the mutual inhibition of hydrogenation by sulfur–organic compounds and hydrogenolysis by aromatics. In our early paper [6], the HAD–HDS problem was studied on the example of benzene hydrogenation and thiophene hydrogenolysis. We have considered an unsteady state kinetic scheme of these reactions on the sulfide (Ni, Mo) and (Ni, W) catalysts. However, that scheme did not take into account a decrease in the HDA activity that appears when thiophene is absent in the reaction mixture for a long period of time.

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Nomenclature

$a = G_{\mathrm{cat}} N_{\mathrm{Ni}} / V_{\mathrm{g}} C_{\mathrm{Tot}}$	parameter in mathematical model
$C_{\mathrm{B}}, C_{\mathrm{H}}, C_{\mathrm{S}}, C_{\mathrm{Th}}$	mole fractions of benzene, hydrogen, H_2S and thiophene in the gas phase
C_i^{f}	mole fraction of components in the feed flow
C_{Tot}	total amount of moles in the gas at the reaction conditions (mmol cm^{-3})
G_{cat}	catalyst loading (g)
k_i	rate constants (min^{-1})
N_{d}	number of components on the catalyst surface
N_{g}	number of the reactants' components in the gas phase
N_{r}	number of the reaction steps
N_{Ni}	amount of Ni in the catalyst (mmol g^{-1})
r_i	rate of reaction steps (min^{-1})
X	conversion of benzene
V_{g}	reactor void volume (cm^3)
w	total gas flow rate (cm^3 min^{-1})

Greek symbols

ν_{ki}	stoichiometric coefficient
$\theta_{\mathrm{B}}, \theta_{\mathrm{S}}$	surface fractions of benzene and H_2S, respectively
τ	contact time in reactor (s)
τ_{g} $(= V_{\mathrm{g}}/w)$	residence time of the reactor (min)

The goal of this work is to develop an unsteady state kinetic model of benzene hydrogenation taking into account the influence of thiophene in the feed gas and modelling the periodic reactor operation.

2. Experimental

The benzene hydrogenation was studied in an isothermal reactor with the fixed catalyst bed [7]. Dihydrogen was passed through a saturator filled either with pure benzene or with a mixture of benzene and thiophene in the molar ratio 9:1. After being loaded into the reactor, the catalyst was treated with a benzene + thiophene mixture until the benzene conversion became constant. Then, the hydrogen + benzene + thiophene flow was replaced by a flow of hydrogen + benzene or hydrogen + benzene + thiophene, in which the molar ratio of benzene/thiophene was varied from 22:1 up to 140:1. The conversion of benzene into cyclohexane was monitored chromatographically at the reactor outlet. The experimental conditions were as follows: $T = 300\,^\circ\mathrm{C}$, $P = 2\,\mathrm{MPa}$, contact time τ was equal to 0.1–0.5 s. The (Ni, Mo)/Al_2O_3 catalyst contained 2.7% of Ni and 13.9% of Mo.

3. Kinetic model

3.1. Benzene hydrogenation

The proposed kinetic model is based on the following standpoints, which were revealed while studying the benzene hydrogenation on the sulfide catalysts under unsteady-state conditions [8–10]:

1. The active sites of both benzene hydrogenation and thiophene hydrogenolysis are nickel atoms incorporated into sulfide bimetallic species which is the active component of the sulfide hydrotreating catalysts.
2. The Ni atoms are considered as active sites for adsorption and activation of both thiophene and benzene molecules.
3. The active sites are covered with adsorbed molecules of either reagents or reaction products at the catalysis conditions.
4. Heat of adsorption of molecules on the active site is situated in decreasing order: thiophene > hydrogen sulfide > benzene > hydrogen > cyclohexane.
5. Both the benzene hydrogenation and thiophene hydrogenolysis occur involving the interaction of a benzene (thiophene) molecule with three (or four) molecules of hydrogen without desorption of possible intermediates into the gas phase.
6. When hydrogen sulfide is absent in both the gas phase and adsorbed state, the structure-forming sulfur atoms interact with dihydrogen, which leads to a destruction of the active-component structure and to the catalyst deactivation.

In accordance with these standpoints, the developed kinetic scheme of the benzene hydrogenation includes 4 following steps:

$$C_6H_6 + [Z_{H_2S}] \leftrightarrow [Z_{C_6H_6}] + H_2S, \tag{1}$$

$$C_6H_6 + 3H_2 + [Z_{C_6H_6}] \rightarrow [Z_{C_6H_6}] + C_6H_{12}, \tag{2}$$

$$nH_2 + [Z_{C_6H_6}] \rightarrow [Z_X] + nH_2S + C_6H_6, \tag{3}$$

$$nH_2 + [Z_{H_2S}] \rightarrow [Z_X] + (n+1)H_2S. \tag{4}$$

The first step involves an interaction of benzene with the adsorbed hydrogen sulfide with the formation of site $[Z_{C_6H_6}]$, which is active in the benzene hydrogenation. Benzene interacts with gas-phase hydrogen to yield cyclohexane (step 2). In the absence of hydrogen sulfide in the gas phase and on the catalyst surface, dihydrogen from the gas phase can interact with sulfur atoms from the active-component structure. This process involves desorption of hydrogen sulfide into the gas phase and destroys the structure of the active component, i.e., leads to the deactivation of the catalyst (steps 3 and 4). Here, $[Z_X]$ is the active-site structure depleted of n sulfur atoms.

The balance of the active surface sites corresponds to the equation

$$[Z_{C_6H_6}] + [Z_{H_2S}] + [Z_X] = [Z_0],$$

where $[Z_0]$ is the total number of active sites, Ni atoms.

We used the following kinetic equations for reaction steps 1–4:

$$r_1 = k_1 C_{\mathrm{B}} \theta_{\mathrm{S}} - k_{-1} C_{\mathrm{S}} \theta_{\mathrm{B}}, \quad r_2 = k_2 C_{\mathrm{H}} C_{\mathrm{B}} \theta_{\mathrm{B}}, \quad r_3 = k_3 C_{\mathrm{H}} \theta_{\mathrm{B}},$$

$$r_4 = k_4 \theta_{\mathrm{S}} C_{\mathrm{H}^\bullet} - k_{-4} C_{\mathrm{S}} \theta_X$$

This kinetic model is similar to a previously published model [11], but has a remarkable distinction. In our model, it is

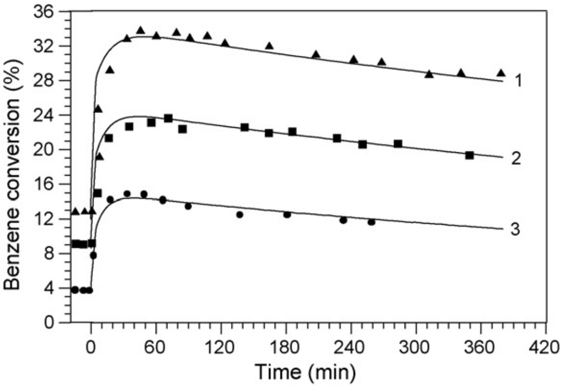

Fig. 1. Benzene conversion versus time at different contact times: (1) $\tau = 0.5$ s; (2) 0.31 s; (3) 0.17 s (points: experiments, lines: simulation).

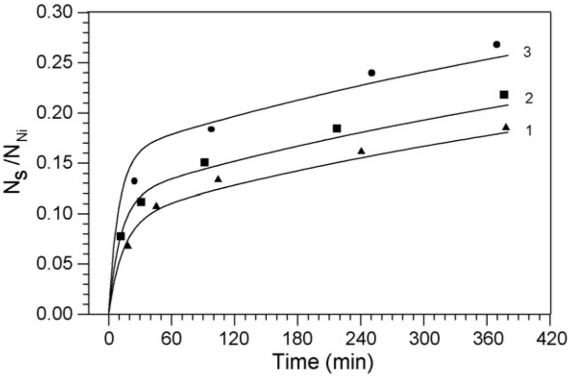

Fig. 2. Dynamics of sulfur storage (atom S/atom Ni) at the reactor outlet at the different contact time: (1) $\tau = 0.5$ s; (2) 0.31 s; (3) 0.17 s (points: experiments, lines: simulation).

supposed that adsorbed cyclohexane desorbs rapidly from the catalyst surface into the gas phase. This allows one to exclude $[Z_{C_6H_{12}}]$ from the balance of the active surface sites.

Taking into account low conversion of benzene, some simulations were performed with the use of the following mathematical model of the continuous stirred tank reactor:

$$\frac{dC_i}{dt} = \frac{1}{\tau_g}(C_i^f - C_i) + a\sum_{k=1}^{N_r} \nu_{ki} r_k(C, \theta),$$

$$\frac{d\theta_j}{dt} = \sum_{k=1}^{N_r} \nu_{kj} r_k(C, \theta), \qquad t = 0: C_i = C_i^0, \quad \theta_j = \theta_j^0,$$

$$i = \overline{1, N_g}, \; j = \overline{1, N_d}.$$

To solve the system of nonlinear differential equations, which describes the balance correlation of the components in the gas phase and on the catalyst surface, we used the semi-implicit method of Runge–Kutta to integrate a set of the stiff ordinary differential equations.

Fig. 1 shows the experimental points and the calculated curves of the benzene conversion versus time at different contact times τ. The catalyst in the reactor was preliminary treated with a mixture of hydrogen + benzene + thiophene (with the benzene to thiophene molar ratio 9:1) until the steady-state conversion was achieved. Note that a considerable part of the active sites is covered with hydrogen sulfide due to a relatively high rate of hydrogenolysis and almost complete thiophene conversion.

At the high content of thiophene in the reaction mixture, the active sites are covered mainly with adsorbed hydrogen sulfide. Therefore, the benzene conversion is low (the initial point in Fig. 1). However, after passing pure benzene (without thiophene) through the catalyst, the H_2S concentration in the gas phase decreases and dihydrogen from the gas phase interacts with sulfur atoms from an active-component structure, which results in its destruction in accordance with the steps 3 and 4 (Fig. 2).

For this reason, the number of active sites participating in the hydrogenation decreases and the benzene conversion diminishes.

The suggested kinetic model describes well the dynamics of changes in the benzene conversion when the kinetic constants are: $k_1 = 26.6$, $k_{-1} = 32$, $k_2 = 56.3$, $k_3 = 0.0012$, $k_4 = 120$, $k_{-4} = 0.011$ (s^{-1}) and $n = 2$. The first order of the reaction with respect to benzene is supposed. The zero order with respect to hydrogen is supposed because a high excess of dihydrogen in the gas phase.

3.2. Benzene hydrogenation in the thiophene presence

Since thiophene has the highest heat of adsorption of molecules in the mixture considered, it will displace molecules of benzene and hydrogen sulfide on the catalyst surface. Then, one can add the following steps for the thiophene hydrogenolysis to steps 1–4:

$$(n+1)C_4H_4S + (3n+4)H_2 + [Z_X] \rightarrow [Z_{H_2S}] + (n+1)C_4H_{10}, \qquad (5)$$

$$C_4H_4S + 4H_2 + [Z_{C_6H_6}] \rightarrow [Z_{H_2S}] + C_4H_{10} + C_6H_6, \qquad (6)$$

$$C_4H_4S + 4H_2 + [Z_{H_2S}] \rightarrow [Z_{H_2S}] + C_4H_{10} + H_2S. \qquad (7)$$

The following kinetic equations for reaction steps 5–7 were used:

$$r_5 = k_5 C_{Th} C_H \theta_X, \quad r_6 = k_6 C_{Th} C_H \theta_B, \quad r_7 = k_7 C_{Th} C_H \theta_S,$$

where C_T is the concentration of thiophene in the gas phase.

Fig. 3 shows the benzene conversion versus time at different benzene/thiophene molar ratios in the feed mixture. The catalyst in the reactor was preliminary treated with a mixture of hydrogen + benzene + thiophene until the steady-state conversion was achieved. One can see that the maximum value of the benzene conversion increases with a decrease in the thiophene concentration. Therefore, the benzene hydrogenation is strongly inhibited by thiophene, which is present in the feed mixture.

Fig. 4 shows the calculated surface concentrations, namely, the fractions of inactive sites and active sites on the catalyst surface covered by reagents. The reaction conditions correspond to Fig. 3. As one can see, the concentration of the sites occupied by benzene, which is active in the HDA process, decreases with the decrease in the ratio of benzene/thiophene. Due to a shift of

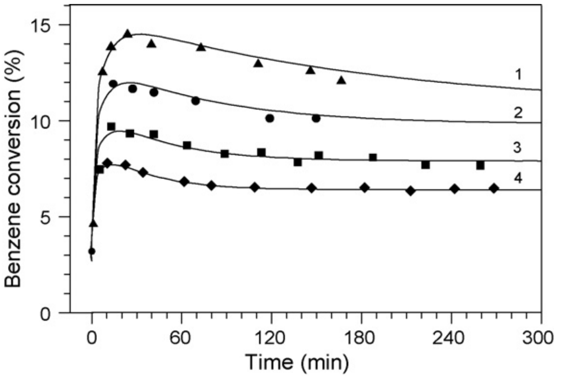

Fig. 3. Benzene conversion versus time at different benzene/thiophene molar ratios in the feed mixture: (1) 140; (2) 50; (3) 35; (4) 22. $\tau = 0.18$ s (points: experiments, lines: simulation).

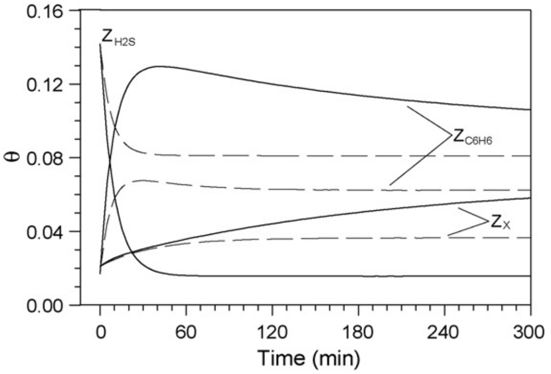

Fig. 4. Fractions of the active sites θ, covered by benzene, hydrogen sulfide and inactive sites Z_X at different benzene/thiophene molar ratios in the feed mixture. $\tau = 0.18$ s. The benzene/thiophene ratio is equal to 140 (solid lines), 22 (dash lines).

equilibrium of the reversible reaction toward benzene formation (step 1), the benzene conversion decreases.

The dependence of the benzene conversion on the replacement of the hydrogen + benzene flow by the flow of hydrogen + benzene + thiophene (the ratio of benzene/thiophene is equal to 9) is shown in Fig. 5. After adding thiophene to the reaction mixture, the benzene conversion decreased sharply and then, after 10–20 min, the conversion attained its new steady-state value.

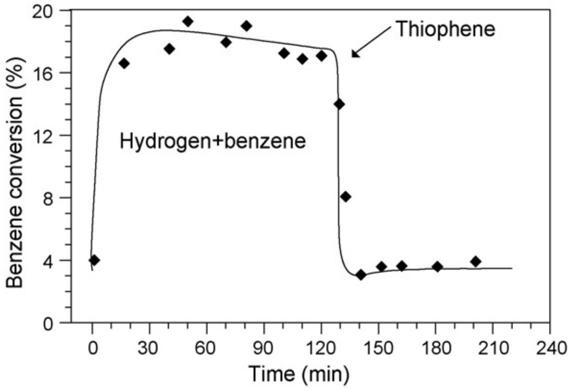

Fig. 5. Benzene conversion versus time after a stepwise feeding of thiophene to hydrogen + benzene flow at $t = 125$ min. $\tau = 0.22$ s (points: experiments, lines: simulation).

The experimental data were best described at the following rate constants of steps 5–7: $k_5 = 800$, $k_6 = 36{,}600$, $k_7 = 1000\,(\mathrm{s}^{-1})$.

The rate of the thiophene hydrogenolysis is essentially higher than that of the benzene hydrogenation. Therefore, under the steady-state conditions, the thiophene conversion is close to 100% while the benzene conversion is rather low. This fact is in a good agreement with experiments.

4. Periodic operation

At carrying out of reaction of the hydrogenation of benzene in the absence of thiophene in a feeding mixture, conversion of benzene eventually tends to decrease at various contact times (Fig. 1). Finally, the conversion of benzene will be practically zero. On the other hand, at high concentration of thiophene, the active sites in hydrogenation of benzene will be blocked by H_2S, because they have stronger adsorption abilities in comparison with benzene. Thus, the stationary conversion of benzene will tend to zero also. Hence, there is an optimum concentration of thiophene at which the maximal steady-state reaction rate of hydrogenation of benzene is reached.

Fig. 6 shows (solid lines), that the maximal steady-state conversion of benzene is reached in the range of the benzene/thiophene ratio equal to 50–150. At increase of the contact time the maximum of conversion becomes more strongly pronounced. The maximal steady-state conversion of benzene is proportional to concentration of sites $Z_{C_6H_6}$, which is defined by a presence of two factors—blocking of the active sites by hydrogen sulphide due to its adsorption and deactivation of the active sites as a result of loss of the sulfur atoms. The maximal transient conversion of benzene has higher value, which depends on contact time (Fig. 6). It follows from the obtained data, that if to treat the catalyst periodically by a mixture containing high concentration of the thiophene, in this case it will be more active under unsteady state operation. One of the ways

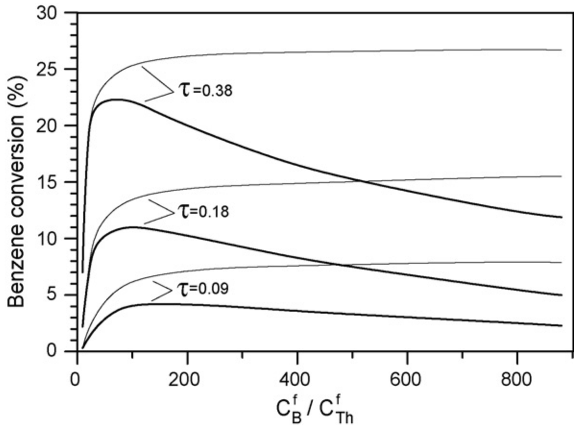

Fig. 6. Dependence of steady-state conversion (solid line) and maximal transient conversion (dash line) on the benzene/thiophene ratio in the feed at the different contact time: (1) 0.38 s; (2) 0.18 s; (3) 0.09 s.

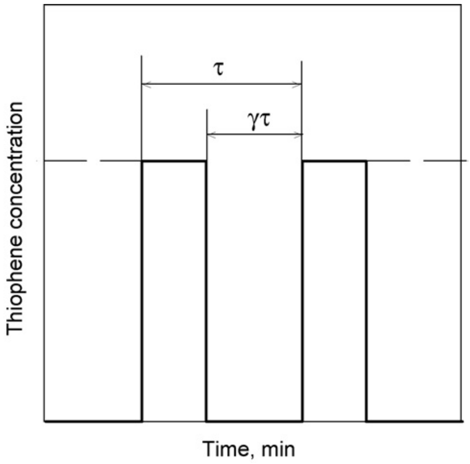

Fig. 7. Schematic presentation of the thiophene concentration variation at a reactor inlet. t_c, period (cycle) time and γ, period split.

to attain the catalyst unsteady state is cyclic oscillations of the reactant concentrations (cyclic reactor operations).

The reactant concentration in the reactor feed is periodically varied in the form of a square wave function as presented in Fig. 7. In the first part of a period, the concentration corresponds to the hydrogen + benzene mixture and then, the flow was replaced by a flow of hydrogen + thiophene (or hydrogen + benzene + thiophene) in the second part of a period. The split between the two parts of a period is defined by the parameter γ. For $\gamma = 0$, the reactor is operated under steady-state with a constant feed concentration.

Fig. 8 demonstrated the average conversion under cyclic mode as a function of period split at the different contact time and various duration of the time of period (t_c). The average conversion of thiophene (X_C) within the first (X') and second part of the period (X'') is given by:

$$X' = \frac{1}{(1-\gamma)t_c}\int_0^{(1-\gamma)t_c} X(t)\,\mathrm{d}t, \quad C_{Th} = 0,$$

$$X'' = \frac{1}{\gamma t_c}\int_0^{\gamma t_c} X(t)\,\mathrm{d}t, \quad C_{Th} = C^0_{Th},$$

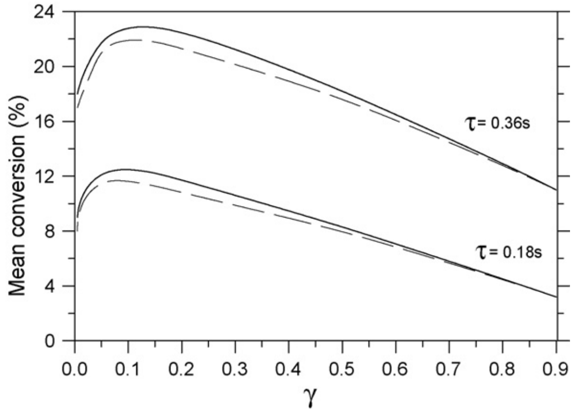

Fig. 8. Average conversion under cyclic mode as a function of period split at the different contact time and period time. $C_B/C_{Th} = 9{:}1$. Solid lines: $t_c = 300$ min; dash lines: $t_c = 600$ min.

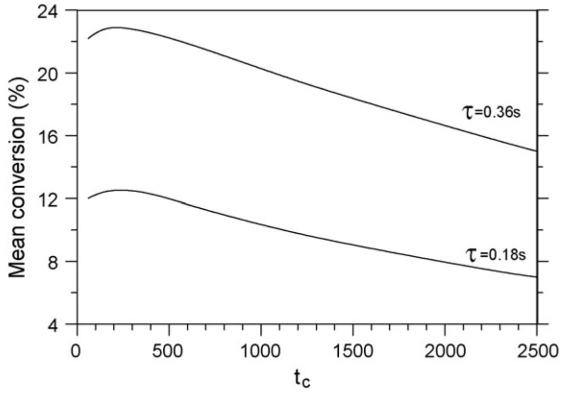

Fig. 9. Average conversion under cyclic mode as a function of period time at the different contact time. $\gamma = 0.1$ and $C_B/C_{Th} = 9{:}1$.

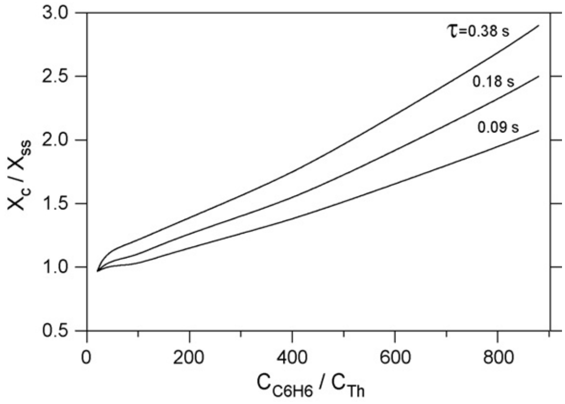

Fig. 10. Dependence of average benzene conversion increasing at cyclic mode on ratio benzene/thiophene in the feed at the different contact time. $t_c = 300$ min; $\gamma = 0.1$; $C_B/C_{Th} = 9{:}1$.

The overall reaction rate during a period is:

$$X_C = X'(1-\gamma) + X''\gamma.$$

It follows from Fig. 8 that the benzene conversion is a function of period split for different cycle times. For $\gamma \rightarrow 0$ and $\gamma \rightarrow 1$, the conversion tends to the steady state value which corresponds to absence or presence of the thiophene in the feeding mixture. As we can see the maximal conversion is attained at the cycle split equal is ~0.1, and the length of forced oscillations period in the reactor consists of ~300 min (Fig. 9). As a result of more active catalyst state, under periodic reactor operation an average conversion was up to several times higher than the steady state value (Fig. 10).

5. Conclusion

The kinetic model of both HDA and HDS reactions on the (Ni, Mo)/Al_2O_3 catalyst has been developed under the assumption that the catalyst surface contains only one type of the active sites – nickel atoms incorporated in a sulfide bimetallic complex – on which the reactions of the C–S bond hydrogenolysis and benzene hydrogenation occur. The number of the active sites decreases due to both the interaction of the network-forming sulfur atoms with dihydrogen and the destruction of the active-site structure.

The model describes adequately the experimental data obtained at the pressure 2 MPa, temperature 573 K and at various contact times and ratios of benzene/thiophene in the feed mixture.

On the base of the kinetic model, the theoretical analysis of the reactor performance under unsteady state conditions was carried out. The unsteady state conditions on the catalyst surface are supposed to be created by forced oscillations of concentration of thiophene in the reactor inlet. The influence of various parameters like cycle split, length of forced oscillations period in the reactor was investigated with respect to the conversion of the benzene. The optimal cycle split is 0.1, the length of forced oscillations period in the reactor consists of ∼300 min. It is shown that under periodic reactor operation an average benzene conversion can be up to several times higher than the steady state value.

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