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Liquid-phase hydrogenation of diethylbenzenes

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Abstract

Hydrogenation of diethylbenzenes in the liquid phase was studied at 358–418 K and 2–6 MPa over 16.7% Ni/Al_2O_3. The reactivity of diethylbenzene isomers was dependent on the mutual position of the substituents and decreased in the following order: 1,3- > 1,4- > 1,2-. The apparent activation energies were ca. 60 kJ/mol. The *cis*-to-*trans* ratio of the corresponding saturated products exhibited only a weak dependence on temperature and hydrogen pressure.

Keywords: Liquid-phase hydrogenation; Alkylaromatic hydrocarbons; Ni catalyst

1. Introduction

Hydrogenation of aromatic hydrocarbons has become a key process for the production of environmentally acceptable transportation fuels in the recent years. As soon as the connection between aromatics and formation of harmful emissions was recognized, tighter environmental regulations were imposed on gasoline and diesel fuel compositions [1–3]. The reduction of aromatics content in diesel results in an improved quality of the fuel since aromatics, owing to their stability, are not suitable for combustion in ignition engines. In addition, the saturation of aromatic hydrocarbons brings further benefits: the cetane number is increased and the fuel density decreased [2,3]. The improvement of these properties has been shown to suppress formation of particulate matter and NO_x emissions [4,5], which are connected with serious health risks [4,6].

Hydrogenation of aromatics has been studied by many researchers both in the liquid and gas phase [7–11]. The studies deal mainly with such aromatics as benzene, toluene and xylenes, in order to shed more light on the mechanistic aspects of the hydrogenation. Since the kinetics of hydrogenation of the aromatic ring depends on the number and the chain length of alkyl-substituents [2,3], investigation of other aromatics (di- or tri-substituted) is needed for a better understanding of the hydrogenation of aromatics in diesel fuels [3]. However, such studies are very scarcely reported in the literature [12].

This study focuses on the investigation of the kinetics of diethylbenzenes hydrogenation over 16.7% Ni/Al_2O_3. Similar catalyst was used in the literature [7,8,12] with other aromatics enabling, thus, a straightforward comparison of hydrogenation of diethylbenzenes with these aromatics. However, attention has to be paid to sulfur content of the fuel. If sulfur is present in the feed to be hydrogenated, it has to be removed prior to hydrogenation to avoid rapid catalyst deactivation. The reaction rates and activation energies for the individual diethylbenzene isomers are reported. The stereoselectivity of the hydrogenation is discussed as well.

2. Experimental

The experiments were performed in a 300-ml electrically heated batch reactor (Parr Industries) using a mixture of diethylbenzenes (1,3-: 64.5%, 1,4-: 30.0%, 1,2-: 4.0%, Fluka, $\geq$95%) and hydrogen (99.999%) as the raw materials. A commercial nickel-alumina catalyst—16.7% Ni/Al_2O_3 (Crosfield)—was employed in the reaction. The catalyst has been extensively characterized previously (BET specific surface area: 108 m^2/g, specific metal surface: 87 m^2/g_{Ni}, metal dispersion: 16%) [13,14]. The catalyst was reduced in situ in flow of hydrogen for 2 h at 673 K prior to the

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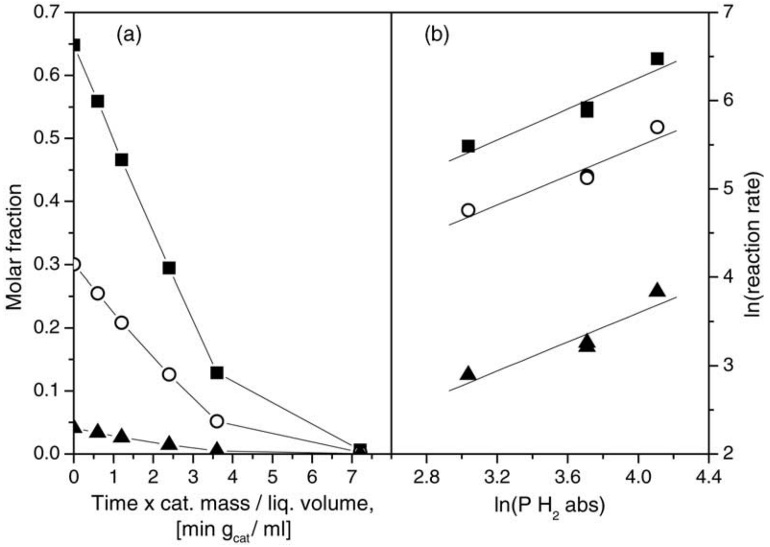

Fig. 1. The consumption of diethylbenzenes (a) and the dependence of the reaction rate on hydrogen pressure (b) at 398 K; 1,3-diethylbenzene (■), 1,4-diethylbenzene (○), 1,2-diethylbenzene (▲).

hydrogenation experiments. The effects of temperature and hydrogen pressure on the rate of diethylbenzenes hydrogenation were investigated in the ranges 358–418 K and 2–6 MPa, correspondingly. To eliminate the interference of the internal and external diffusion, very fine catalyst particles (<63 μm) were used and vigorous stirring was applied (1500 rpm). Values of effectiveness factor (=0.9999) and hydrogen concentration difference between the liquid bulk and particle surface (4×10^{-9} mol/cm^3) calculated according procedure described in [15] prove that the effect of internal and external diffusion limitations on the reaction is negligible. Experiments with different catalyst amounts (3 and 6 g) confirmed that the gas-to-liquid mass transfer did not, under the experimental conditions, limit the reaction. The reaction products were analyzed with a gas chromatograph (Agilent 6890N) equipped with a non-polar capillary column (DB-Petro 100 m × 0.2 mm × 0.5 μm) and a FI detector. The experimental error including product analysis was estimated to be less than 5%.

3. Results and discussion

The mixture of diethylbenzenes was selectively converted into a mixture of corresponding diethylcyclohexanes in course of the reaction. The butylbenzenes present as an impurity in concentration equal to 1.5 mol% yielded corresponding butylcyclohexanes. Diethylcyclohexenes, possible reaction intermediates of the hydrogenation, were observed in negligible concentrations and only during the initial phase of the reaction. Their total concentration did not exceed 0.5 mol%. Total conversion of all aromatics was achieved for all experiments but one at 358 K within 6 h. The reaction rate has increased with the increasing temperature and the increasing pressure of hydrogen.

A typical profile of the diethylbenzenes consumption is shown in Fig. 1a. It can be observed that the concentration of all diethylbenzene isomers exhibits a linear dependency on the reaction time up to high conversions levels (Fig. 1a). This means that the reaction order with respect to any of the diethylbenzenes is equal to zero, i.e., the reaction rate is independent of the aromatics concentration. Similar behavior was reported previously for liquid-phase hydrogenation of other aromatic hydrocarbons [2,7,8,12,16]. The zeroth order dependence on the concentration of aromatics was ascribed to a very high surface concentration of these compounds due to their strong adsorption on the active sites [2]. The hydrogenation rate is, however, influenced by the hydrogen partial pressure. The dependency of the hydrogenation rate as a function of hydrogen pressure (Fig. 1b) reveals that the reaction order with respect to hydrogen for the individual diethylbenzenes lies in the range 0.8–0.9. When comparing the individual isomers, only small differences can be found (Table 1). The reaction orders with respect to hydrogen determined here for diethylbenzenes are similar to those reported for hydrogenation of toluene and xylenes in liquid phase [7,8,12]. Furthermore, no effect of temperature on these partial reaction orders could be found in this study.

The activation energies for the hydrogenation of the individual isomers have been calculated based on the measured reaction rates in the range 358–418 K at 4 MPa and are reported in Table 1. Rather small differences among the isomers can be observed. The highest activation energy (59.8 kJ/mol) observed for 1,3-diethylbenzene is just 1.8 kJ/mol higher than the lowest one (58.0 kJ/mol) found for 1,2-diethylbenzene. These values are higher than the ones reported for the hydrogenation of xylenes in gas [11] and liquid phase [12]. Moreover, the activation energies of the hydrogenation of the individual dimethylbenzenes (50–

Table 1
Kinetic parameters for the liquid-phase hydrogenation of the diethylbenzenes mixture

Reactants	Reaction order with respect to		Activation energy[a] (kJ/mol)	TOF[b] ($s^{-1} \times 10^3$)
	Aromatic	Hydrogen[a]		
1,2-Diethylbenzene	0	0.82 ± 0.23	58.0 ± 1.3	2.9
1,3-Diethylbenzene	0	0.88 ± 0.19	59.8 ± 1.2	36.1
1,4-Diethylbenzene	0	0.83 ± 0.19	59.0 ± 1.0	17.4

[a] With 95% confidence interval.
[b] At 398 K and 4 MPa.

57 kJ/mol [11], 35–52 kJ/mol [12]) differ from each other more than the values found for diethylbenzenes.

The hydrogenation rates of the individual diethylbenzenes in their mixture were found to depend on the mutual position of the ethyl substituents and decreased in the order: 1,3-diethylbenzene > 1,4-diethylbenzene > 1,2-diethylbenzene. This finding is in contrast with the results previously reported for gas- and liquid-phase hydrogenation of xylenes (activity order: 1,4-dimethylbenzene ≥ 1,3-dimethylbenzene > 1,2-dimethylbenzene) [11,12] and indicates that the chain length of the substituents affects the relative order of the reactivity of di-substituted alkylbenzenes, most probably due to the steric effects. It should be noted that the reaction rates reported here are apparent, i.e., they include adsorption coefficients. Since the experiments were performed with a mixture of diethylbenzenes, competitive adsorption of the individual isomers can be expected.

The presence of two substituents opens a possibility for formation of two stereoisomers (*cis* and *trans*) as a result of the aromatic ring saturation. The *cis*-to-*trans* ratio is influenced by the difference in the rate of formation of *cis*- and *trans*- isomers (i.e., by kinetics) and by the conformational stability of a particular *cis*- or *trans*-isomer (i.e., by thermodynamics). It is generally known that the *cis*-isomer is more stable for 1,3-substituted cyclohexanes whereas *trans*-isomers are preferred in the case of 1,2- and 1,4-substituted cyclohexanes [17]. The *cis*-to-*trans* ratios equal to 3.48 and 0.29 for 1,3- and 1,4-diethylcyclohexanes, respectively, were measured by Allinger and Hu [18] at 530 K.

Different rates of formation of *cis*- and *trans*-isomers from the respective diethylbenzenes were found in this study. The relative rate of formation of *cis*- and *trans*-diethylcyclohexanes can be determined from the ratio of their concentrations as a function of reaction time for the respective diethylcyclohexanes (i.e., 1,2-, 1,3- and 1,4-). The *cis*-isomers were produced at higher rate in the case of hydrogenation of 1,3-diethylbenzene and 1,4-diethylbenzene (Fig. 2). The *trans*-isomer was the preferred product of 1,2-diethylbenzene hydrogenation (Fig. 2). The values of *cis*-to-*trans* ratios in the range 3.0–3.4, 1.0–1.2 and 0.7–0.8 were found for 1,3-, 1,4 and 1,2-diethylbenzene hydrogenation, correspondingly. On the contrary, in xylenes hydrogenation in liquid phase [12] *cis*-isomer was the prevailing product of 1,2-dimethylbenzene hydrogenation. Similar values of the *cis*-to-*trans* ratio were obtained for the liquid-phase hydrogenation of 1,3-dimethylbenzene [12] and 1,3-diethylbenzene. The hydrogenation of 1,4-dimethylbenzene [12] and 1,4-diethylbenzene yielded almost equal amounts of the *cis*- and *trans*-isomers.

The value of the *cis*-to-*trans* ratio was virtually constant during the course of the reaction for all diethylcyclohexanes (i.e., 1,2-, 1,3- and 1,4-). As no changes in this ratio were

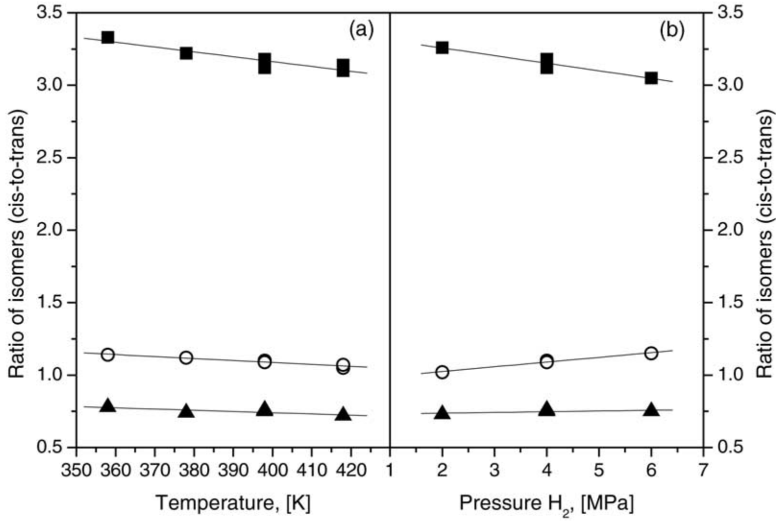

Fig. 2. The dependence of the *cis*-to-*trans* ratio of diethylcyclohexanes on temperature (a) and hydrogen pressure (b); 1,3-diethylcyclohexane (■), 1,4-diethylcyclohexane (○), 1,2-diethylcyclohexane (▲).

observed after complete saturation of all aromatics, it can be concluded that the stereoisomerization did not occur and, thus, the reported *cis*-to-*trans* ratios are a result of the differences in the hydrogenation kinetics and not due to epimerization of diethylcyclohexanes. This conclusion is supported by the thermodynamic data, which were obtained for *cis*-to-*trans* ratio of 1,3- and 1,4-diethylcyclohexane [18] at higher temperatures than the highest temperature used in the present study but could be extrapolated to the temperature domain studied here.

Both temperature and hydrogen pressure affected the *cis*-to-*trans* ratio of the individual diethylcyclohexanes (Fig. 2) only to a minor extent. The *cis*-to-*trans* ratio of all diethylcyclohexanes decreased when the reaction temperature was increased indicating a slight preference for the formation of *trans*-isomers at higher temperatures (Fig. 2a). The temperature dependence of *cis*-to-*trans* ratio can be ascribed to kinetic as well as thermodynamic effects since thermodynamic equilibrium [18] was not reached in the experiments. On the other hand, a different behavior can be observed to result from the increase of the hydrogen pressure (Fig. 2b). While the concentration of *trans* 1,4-isomer decreases with the increasing pressure, an opposite trend is witnessed for *trans* 1,3-diethylcyclohexane (Fig. 2b). The *cis*-to-*trans* ratio of 1,2-diethylcyclohexane seems to be unaffected by the changes in the reaction pressure (Fig. 2b). Different routes to *cis*- and *trans*- isomers can explain the differences in *cis*-to-*trans* ratios due to variations in hydrogen pressure. This has been recently discussed by Neyestanaki et al. [19] for gas-phase hydrogenation of 1,2-dimethylbenzene. It can be concluded that the choice of reaction conditions did not virtually influence the relative rates of formation of *cis*- and *trans*-diethylcyclohexanes. Similar trends were observed in the liquid-phase hydrogenation of xylenes [12].

4. Conclusions

Hydrogenation of diethylbenzenes in the liquid phase was studied at 358–418 K and 2–6 MPa over a Ni catalyst in order to obtain more insight in the kinetic behavior of complex aromatic hydrocarbons, which may be of interest for optimizing the dearomatization of fuels. At the same time, the stereochemistry of the hydrogenation of the individual diethylbenzenes was investigated. The main findings can be summarized as follows.

Ni supported on alumina was found to be an active and selective catalyst already at mild conditions. The reactivity of the individual diethylbenzene isomers was dependent on the mutual position of the substituents and decreased in the following order: 1,3- > 1,4- > 1,2-. The apparent activation energies were for all isomers in the range 58–60 kJ/mol. 1,3-Diethylbenzene yielded *cis*-1,3-diethylcyclohexane in high excess (*cis*-to-*trans* ratio >3). The hydrogenation of the other two isomers (1,4- and 1,2-diethylbenzenes) produced comparable amounts of the corresponding *cis*- and *trans*-diethylcyclohexanes. The *cis*-to-*trans* ratio of the formed diethylcyclohexanes exhibited only a weak dependence on temperature and hydrogen pressure.

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