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Kinetics and modeling of *o*-xylene hydrogenation over Pt/γ-Al_2O_3 catalyst

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Abstract

Gas-phase hydrogenation of *o*-xylene to *cis*- and *trans*-dimethylcyclohexane (DMCH) was studied in a differential microreactor at atmospheric pressure and 430–520 K over a Pt/γ-Al_2O_3 catalyst. Rapid reversible deactivation of the freshly reduced catalyst prompted reactivation before every kinetic measurement and extrapolation of the steady-state activity to initial activity. Reaction orders were close to zero for *o*-xylene and ranged from 1.5 (430 K) to 3.0 (520 K) for hydrogen. A rate maximum for the production of the saturated compounds was observed at about 460 K. The results were in line with previously reported results on xylene hydrogenation on Ni/γ-Al_2O_3 catalyst.

Keywords: *o*-Xylene hydrogenation; Pt/γ-Al_2O_3; Kinetic modeling; Deactivation

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1. Introduction

Catalytic hydrogenation of aromatics is used in oil refining industry to lower the amount of undesired aromatic hydrocarbon in diesel fuels. Therefore, hydrogenation of aromatic compounds over Group VIII metals has attracted considerable interest of researches both from applied and theoretical viewpoint. Benzene hydrogenation is the most frequently studied system as this reaction has also industrial implementation in chemical industry both in gas and liquid phases [1].

Several studies were devoted to catalytic hydrogenation of substituted aromatic compounds such as toluene and more specifically of dialkylbenzenes with the formation of dialkylcyclohexene and *cis*- and *trans*-dialkylcyclohexanes [2–19].

The most intriguing question in elucidating the mechanism of this reaction is the influence of substituents on reaction rate and the origin of the formation of *cis*- and *trans*-dialkylcyclohexanes, since only *cis* is expected if an aromatic molecule is lying flat on the surface.

The rate of aromatic hydrogenation is strongly affected by steric factors as the hydrogenation rate decreases by substitution of alkyl groups to the aromatic ring. The liquid-phase hydrogenation of aromatics has received considerable attention. Toppinen et. al. [3] discussed liquid-phase hydrogenation of different aromatics over nickel catalysts. Following conclusions were made by Toppinen: the reaction rate decreases with increasing length of substituent (benzene > toluene > ethylbenzene > cumene). The reaction rate decreases with increasing number of substituents (benzene ≫ toluene ∼ xylenes > mesitylene). The relative positions of the substituent had a significant effect on the reaction rate, the *para*-position being the most reactive and the *ortho*-position the least reactive (p-xylene > m-xylene > o-xylene).

The kinetics of gas-phase catalytic hydrogenation of xylenes has been investigated over supported Ni, Pd and Rh catalysts [4–15]. For instance, Smeds et al. [4–9] studied hydrogenation of ethylbenzene and xylenes over alumina supported nickel catalysts. The authors investigated the hydrogenation kinetics and observed the rate passing through a maximum at all hydrogen and xylene partial pressures studied. Keane and co-workers [10,12–14] performed the gas-phase hydrogenation of benzene, toluene and xylenes over Ni/SiO_2. Turnover frequencies at a particular temperature was reported to decrease in the order p-xylene > m-xylene > o-xylene. Reaction orders with respect to xylenes were rather close to each other and varied from <0.1 to 0.44 as the temperature was raised from 393 to 523 K. Reaction orders with respect to hydrogen increased with temperature from 0.7 to 2.3 indicating a complex multi-step reaction mechanism. There are fewer data, however, on aromatics hydrogenation over supported platinum catalysts.

Lin and Vannice in a series of communications [16,17], studied the performance of Pt-supported on various supports

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in benzene and toluene hydrogenation. The authors observed a reversible maximum in activity versus temperature in benzene hydrogenation at around 473 K and explained the observation by decrease in the coverage of benzene at higher temperatures. The authors as well reported that the steady state in activity could be achieved quickly after less than 5–10 min. Near to zero reaction orders in benzene hydrogenation was reported. The authors in their study of toluene hydrogenation over supported Pt-catalysts [17] reported the partial pressure dependency of toluene to be around zero and the orders with respect to hydrogen was found to be less than 0.7 at 337 K to over unity at 373 K.

Few studies address the stereoselectivity of xylene hydrogenation over platinum based catalysts. Saymeh and Asfour [18] in their work on the gas-phase hydrogenation of *o*-xylene over Pt/alumina catalyst at temperature ranges of 308–473 K suggested a non-competitive Langmuir–Hinshelwood mechanism. The reaction rate was found to have a maximum at 413 K. The orders with respect to *o*-xylene were reported to be from 0 to 0.28 (308–363 K). The order with respect to hydrogen was observed to be constant at value of 1.22 in the temperature ranges of 308–363 K, whereas, at higher temperatures the order increased to the value of 2.52 (at 413 K).

The same group [19] studied the gas-phase hydrogenation of *o*-xylene over Pt/alumina catalyst. The authors reported an increase toward the selectivity of the thermodynamically favored *trans*-1,2-dimethylcyclohexane (DMCH) by decreased Pt-particle size. The phenomena was explained by the roll-over mechanism. The authors also observed decreased rate of *cis* and consequently increased rate of *trans*-1,2-DMCH formation by temperature (300–340 K). Deactivation at the first 20 min of the run was reported and the steady-state was then achieved.

In the present study, kinetics of gas-phase hydrogenation of *o*-xylene over highly dispersed Pt/alumina catalysts as well as stereoselectivity of the final products at temperature ranges of 430–520 K were investigated. Different characterization techniques were used to correlate the catalytic activity and selectivity as well as the understanding of the surface catalytic chemistry.

2. Experimental

Alumina supported platinum catalysts were prepared by impregnation of a γ-alumina support (LaRoche) having a surface area of 247 m^2/g with solutions of H_2PtCl_6. The catalysts were washed and dried at 353 K. The activity of the catalyst were tested in a continuous flow tube reactor at WHSV of 116 h^{-1} and partial pressures of H_2 and *o*-xylene of 0.19–0.38 and 0.04–0.10 bar, respectively. Argon was used as the make-up gas. Special experiments were carried out to ensure that the kinetics is measured in the absence of external and internal diffusion limitations. Prior to the experiments the dried catalysts (125–150 μm, ca. 60 mg) were reduced in situ in H_2-flow at the pre-set temperature, followed by cooling to the reaction temperature at which point the reactants were introduced to the catalyst. The experimental set-up for the catalyst testing is illustrated in Fig. 1. The flows were controlled by means of mass flow controllers (Brooks). The *o*-xylene (Fluka, >99.5% purity)

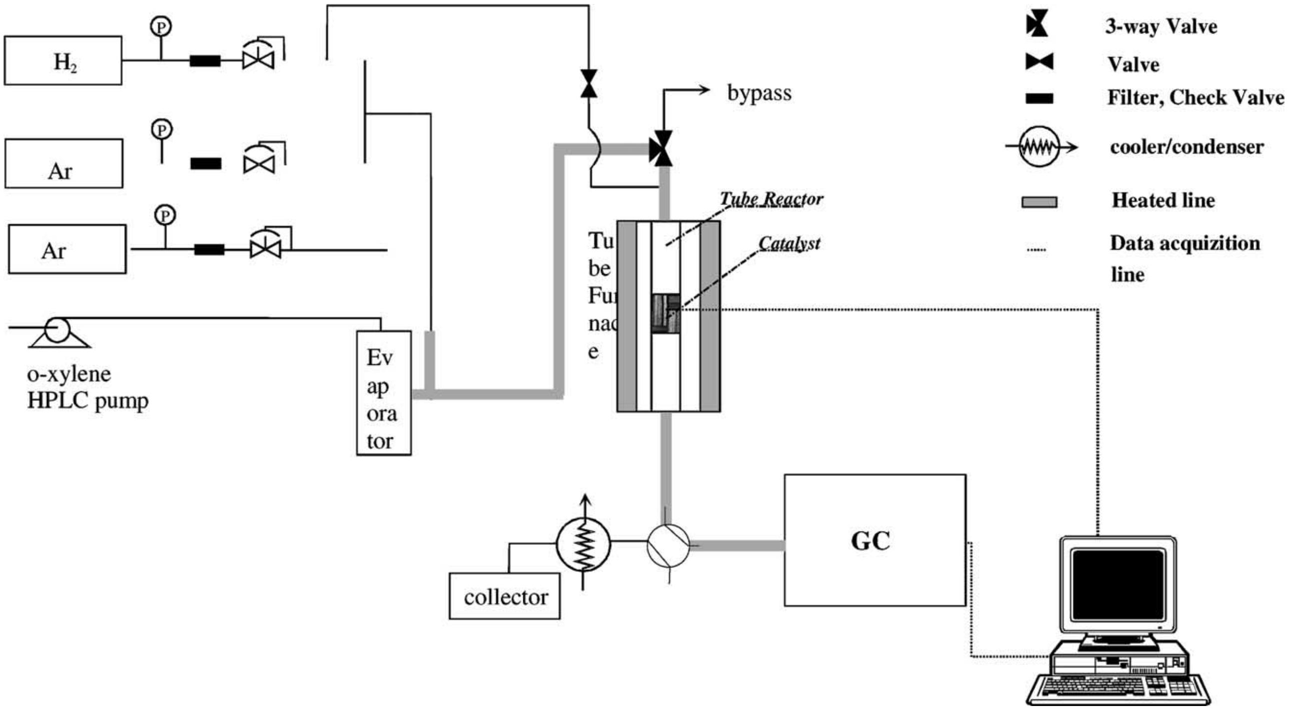


Fig. 1. The experimental set-up for catalyst testing.

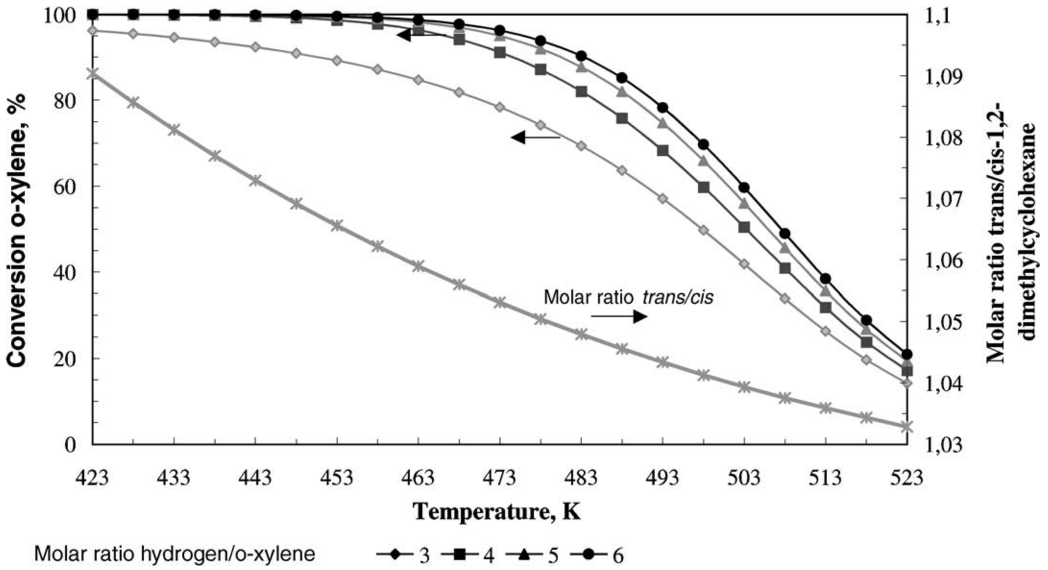


Fig. 2. The thermodynamic calculations for the conditions used.

was pumped using a high performance liquid chromatography (HPLC) pump, evaporated in an evaporator (Bronkhorst) kept at 443 K and was further driven by argon. All the lines after the evaporator and the reactor were heated. All the gases were of the following purity: 99.999 vol.%. The products were analyzed by Varian 1400 GC, equipped with 60 HP-1 column (cross linked methyl siloxane) and FI-detector. The separation was done isothermally (373 K) and the products were further confirmed by GC–MS.

The activity of the catalyst was studied in the temperature range of 430–520 K with 10° intervals. The reaction orders with respect to hydrogen and *o*-xylene were determined by varying the partial pressures from 0.19 to 0.38 and 0.04 to 0.1 bar, respectively.

3. Results and discussion

3.1. Kinetics

The hydrogenation experiments were carried out when the catalyst was reduced at different reduction temperatures, i.e. 573, 623 and 673 K. The highest rate was obtained with catalyst reduced at 673 K, thus, this temperature was selected in kinetics experiments. *cis*- and *trans*-1,2-DMCH were the only hydrogenation products (i.e. no alkylcyclohexene was detected) and their ratio did not significantly change during the initial catalyst deactivation.

The thermodynamic calculation for the gas composition at the operation temperatures used is given in Fig. 2. A typical

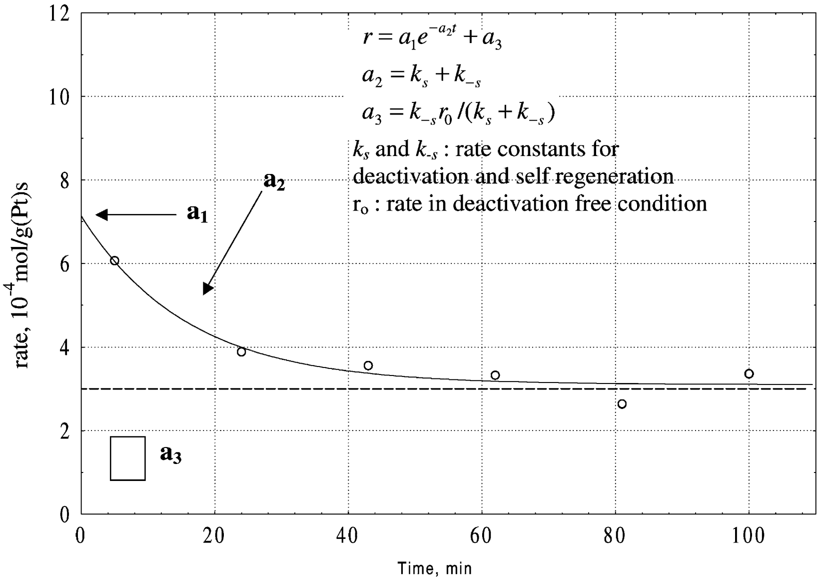


Fig. 3. A typical hydrogenation experiment; $p_{H_2} = 0.36$, $p_{o\text{-xylene}} = 0.06$ bar and $T = 470$ K.

kinetic run is presented in Fig. 3. As shown catalyst deactivation took place during the first 20 min and steady-state operation was reached. The catalyst deactivation will be discussed later. Catalyst deactivation is commonly observed for the reactions involving hydrocarbons and is believed to be a consequence of carbon deposition [20,21]. In the present study, the deactivation was found to be reversible as the hydrogen treatment of the used catalyst at 673 K completely restored the initial catalyst activity. The observed time on-stream deactivation is in good agreement with the data presented in the literature [16,17,19] (see Section 1).

Instead of semi-empirical model for catalyst fouling [22], which was previously applied [4], in the present study a mechanistic deactivation model was applied [23]:

$$r = a_1 e^{-a_2 t} + a_3 \tag{1}$$

where r is the reaction rate, t the time on-stream and a_i the constants,

$$a_2 = k_s + k_{-s}, \qquad a_3 = k_{-s}\frac{r_0}{(k_s + k_{-s})} \tag{2}$$

k_s and k_{-s} are the rate constants for deactivation and self regeneration; r_0 the rate in deactivation free condition.

The coefficient a_3 is representing the rate at steady-state, whereas the reaction rate at time infinitely close to zero can be expressed by the sum of a_1 and a_3.

Fig. 4 represents the hydrogenation rates at steady-state as a function of temperature. The rates passes through a maximum at approximately 460 K. Previously, [18] temperature at which maximum hydrogenation rate in *o*-xylene hydrogenation over Pt was reported to be 413 K. Thermodynamic calculations (Fig. 2) indicate that the experimental data are obtained in the region very far from the equilibrium, therefore, the decrease in the hydrogenation rate above 460 K can be solely attributed to the hydrogenation kinetics.

The temperature dependency of TOF can be explained as a combined effect of an increase in the hydrogenation rate on the catalyst surface and the accompanying decrease in the concentration of surface reactive aromatic species which ultimately result in the formation of $T_{\max}$. Such decrease in xylene surface coverage is in good agreement with the our *o*-xylene TPD experiments, where the peak maximum in *o*-xylene desorption was very close to the temperature of the maximum activity in *o*-xylene hydrogenation.

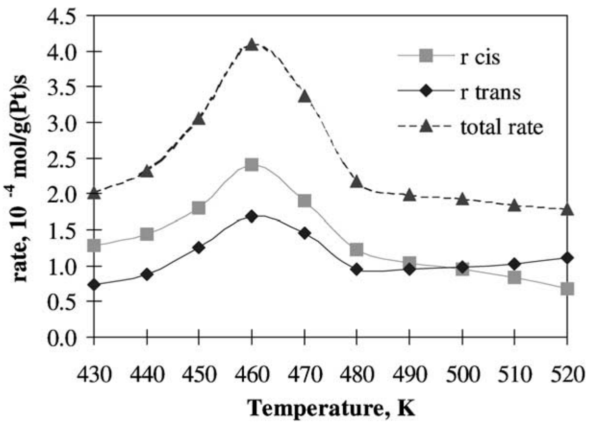


Fig. 4. The rate of *o*-xylene hydrogenation (at steady state) and *cis*-, *trans*-1,2-DMCH formation at different temperatures; $p_{H_2} = 0.36$ and $p_{o\text{-xylene}} = 0.06$ bar.

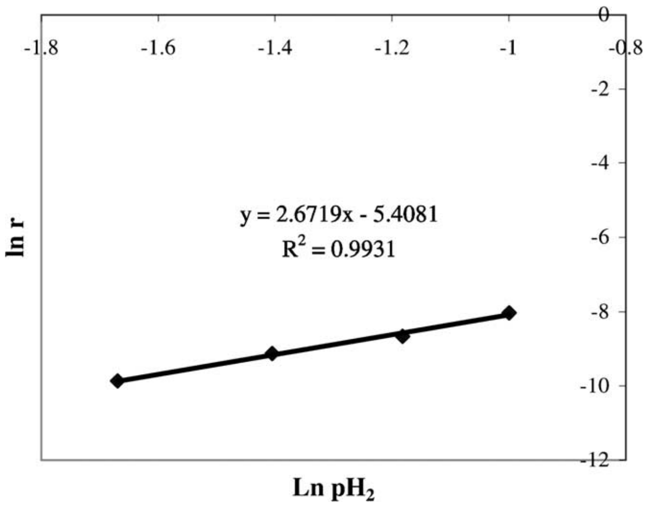


Fig. 5. Dependency of reaction rate at steady state on hydrogen partial pressure, $T = 470$ K, $p_{o\text{-xylene}} = 0.06$ bar.

The rates at steady-state was used for the determination of the kinetic data. The reaction orders in hydrogen and *o*-xylene partial pressures were determined in temperature ranges of 430–520 K with intervals of 10 K. The orders in *o*-xylene were found to be close to zero at all the temperatures investigated. The order in hydrogen partial pressure (Fig. 5) increased with temperature from 1.5 at 430 K to 3 at 520 K (Table 1), suggesting decreased hydrogen coverage by increased temperature. The result indicated an increased *cis*/*trans*-1,2-DMCH ratio by increased hydrogen concentration. On the other hand, the *cis*/*trans* ratio decreased by increased operation temperature (Fig. 6). As shown in Fig. 2, *trans*-1,2-DMCH is thermodynamically favored (if the ratio *trans*/*cis* corresponds to thermodynamic, it should be not less than 4.5 for *o*-xylene even at highest *T*) and as shown in

Table 1
Experimentally determined reaction orders with respect to hydrogen, *trans*- and *cis*-1,2-DMCH[a]

Temperature (K)	n_{H_2}	α_{cis}	α_{trans}	a
430	1.56	1.709	1.335	2.57
440	1.76	1.761	1.471	2.29
450	2.10	2.178	1.995	1.72
460	2.34	3.026	2.482	2.72
470	2.67	2.738	2.593	1.49
480	2.36	2.566	2.326	1.64
490	2.38	2.457	2.308	1.27
500	2.70	2.723	2.687	1.01
510	2.77	2.754	2.779	0.81
520	2.99	2.913	2.800	0.63

[a] $p_{H_2} = 0.19 - 0.36$, $p_{o\text{-xylene}} = 0.4 - 0.1$ bar; $m_{o\text{-xylene}} = 0$.

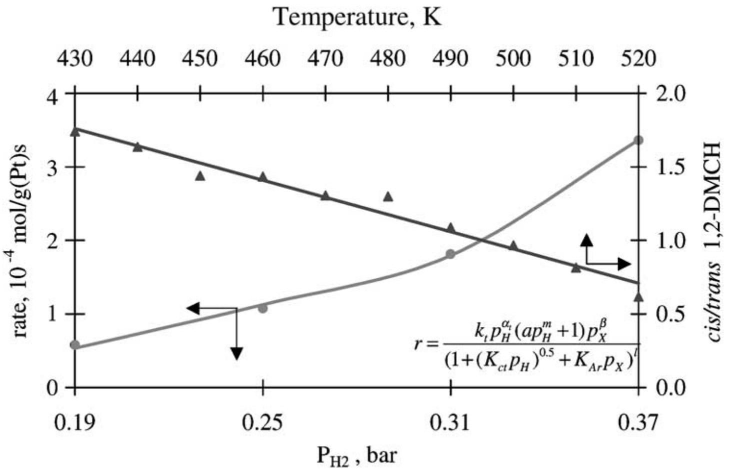


Fig. 6. The effect of temperature and hydrogen partial pressure on the steady state hydrogenation rate ($p_{o\text{-xylene}} = 0.06$ bar, $T = 470$ K) and *cis*/*trans*-1,2-DMCH ratio ($p_{H_2} = 0.36$ bar, $p_{o\text{-xylene}} = 0.06$ bar).

Fig. 6, the *cis* stereoisomer is kinetically favored. As mentioned, the hydrogenation rate at any given temperature was found to increase with increased hydrogen partial pressure. The *cis*/*trans* ratio as well increased with hydrogen partial pressure (Fig. 7).

Previously, it was shown that the xylene hydrogenation rate is passing through a reversible maximum over alumina supported Ni-catalyst [4], which is in good agreement with the present study. *trans*-1,2-DMCH was found to be the dominant product, moreover cycloolefin was formed, although at a rate one order of magnitude lower than the rate of main product formation. For Ni catalyst [4] stereoselectivity in *o*-xylene hydrogenation also depended on T and partial pressure of reactants. Selectivity to *trans* increased with T increase up to a certain value after which no further increase was observed [4].

The initial reaction rates in hydrogenation of substituted xylenes were previously modeled [8] applying a general type of power-law rate equation [24]:

$$r = \frac{k p_H^m p_H^n}{(1 + K_1 p_M + K_2 p_H)^l} \tag{3}$$

with an Arrhenius type of temperature dependence of k and K_i.

In the present communication, Eq. (3) was modified to account explicitly for formation of two stereoisomers and for dissociative adsorption of hydrogen

$$r = \frac{(k_c p_H^{\alpha_c} + k_t p_H^{\alpha_t}) p_X^\beta}{(1 + (K_{ct} p_H)^{0.5} + K_{Ar} p_X)^l} \tag{4}$$

or

$$r = \frac{k_t p_H^{\alpha_t} (a p_H^m + 1) p_X^\beta}{(1 + (K_{ct} p_H)^{0.5} + K_{Ar} p_X)^l} \tag{5}$$

where p_X is the *o*-xylene pressure, $a = k_c/k_t$ (Table 1) and $m' = \alpha_c - \alpha_t$ are obtained from the intercept and slope of

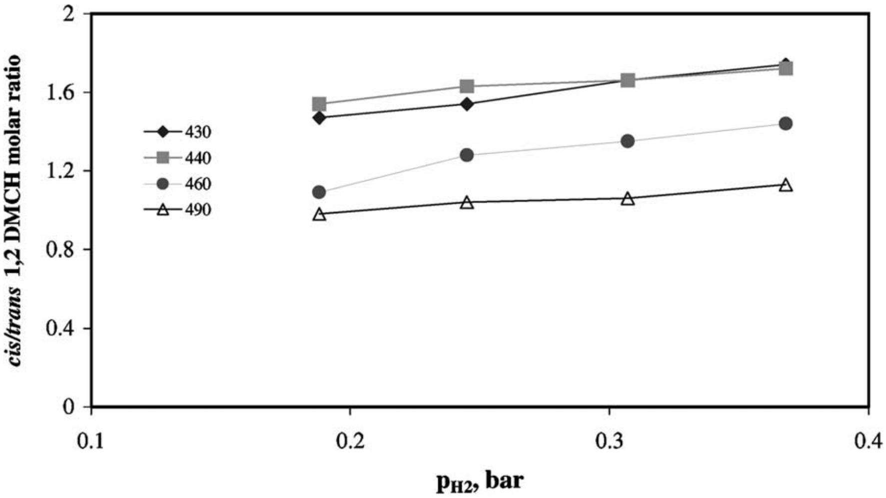


Fig. 7. The effect of hydrogen partial pressure *cis*/*trans* 1,2-DMCH ratio, $p_{o\text{-xylene}} = 0.06$ bar.

Table 2
The estimated parameters from Eq. (5) at some temperatures

Temperature (K)	K_{ct}	K_{Ar}	k
440	3.0×10^8	2.2×10^5	2.5×10^{-8}
460	1.2×10^8	5.8×10^5	6.9×10^{-8}
480	5.6×10^7	1.4×10^6	1.7×10^{-7}
490	3.9×10^7	2.0×10^6	3.0×10^{-7}
500	2.7×10^7	3.0×10^6	4.7×10^{-7}
510	1.9×10^7	4.2×10^6	7.5×10^{-7}

the $\ln(r_c/r_t)$ versus $\ln p_{H_2}$. In fact k_t in Eq. (5) is an apparent rate constant, as it includes also adsorption coefficients of hydrogen and *o*-xylene. The parameter estimation for Eq. (5) was performed [25] for the whole temperature range together assuming an Arrhenius and van't Hoff type of temperature dependences for k and K, the parameters estimated are given in Table 2. The following values of parameters were also obtained $\alpha_t = 2.42$, $b = 1.13$, $l = 1.46$. Generally rather good fit was obtained (Fig. 8) with the degree of explanation 93%. The structure of this simplified model prevents from detailed discussion of the physical reasonability of the calculated parameters, which should be done only for the calculated parameters, which are based on a sound mechanistic model.

It is interesting to note, that deactivation pattern also followed quite distinct temperature dependence. The plot of a_2 versus temperature is presented in Fig. 9. It is immediately clear, that a_2 follows the same pattern as activity does. As can be seen from Eq. (2), a_2 represents the so referred "steepness of deactivation". The similar pattern of the a_2 to the temperature dependency of hydrogenation rate is believed to be due to an increase of carbon deposition on the platinum as with the increased TON the probability of carbon deposition is higher.

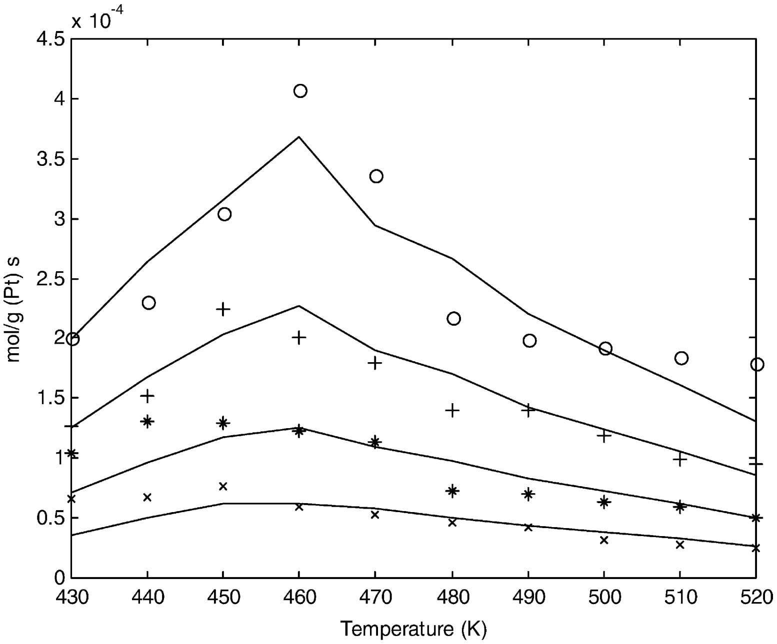


Fig. 8. The rate dependency on temperature at different hydrogen partial pressures ($p_{o\text{-xylene}} = 0.06$ bar). Lines: fit to the model. (○); $p_{H_2} = 0.36$ bar; (+): $p_{H_2} = 0.30$ bar; (✱): $p_{H_2} = 0.24$ bar; (×): $p_{H_2} = 0.19$ bar.

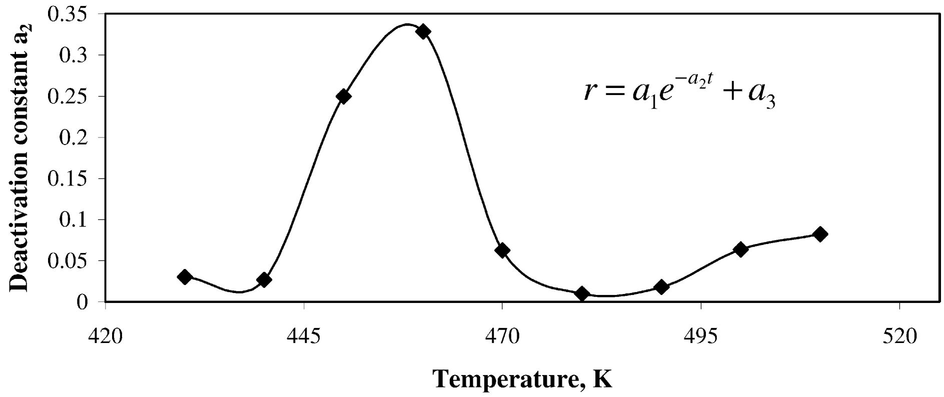


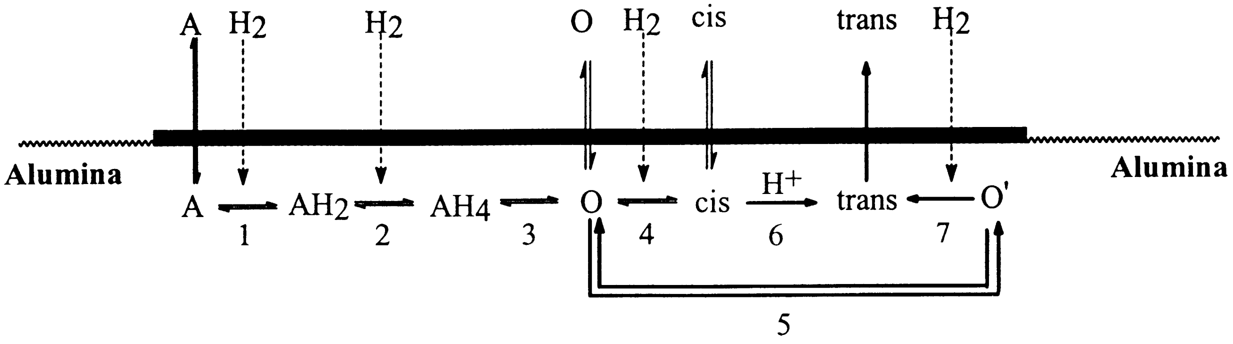
Fig. 9. The "steepness" of catalyst deactivation (a_2) dependency on the reaction temperature, $p_{H_2} = 0.36$, $p_{o\text{-xylene}} = 0.06$ bar.

4. Reaction mechanism

The kinetics observed in *o*-xylene hydrogenation over Pt resembles very closely the kinetics in xylenes hydrogenation [7,8] on Ni catalyst. The general power-law rate equation, was successfully applied for the description of *o*-xylene hydrogenation on Pt in this study, was previously capable of describing the same reaction on Ni.

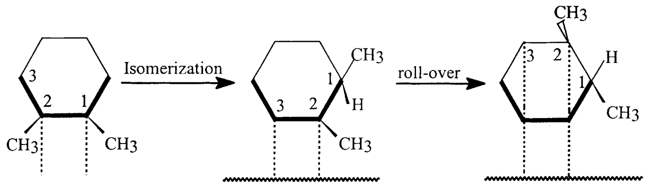
This equation, although a simplified one captures the main features of reaction kinetics, namely the reaction orders towards reactants and the temperature dependence.

Thus, we have the reason to believe that the mechanistic model suggested previously for Ni applies also in the present case. The proposed model features fast adsorption of the reactants and rate determining surface addition of hydrogen atom pairs to the aromatic molecule, the first two addition steps giving rise to a cyclic olefin which through its adsorption–desorption behavior governs the stereochemical distribution [26] according to the following scheme:



where A and AH_i denote the aromatic hydrocarbon and the partially hydrogenated surface intermediates and O is the substituted cyclic olefin (either in *cis* or in *trans* form). The surface intermediate AH_4 isomerizes into adsorbed cyclic olefin (precursor for *cis* cyclic olefin in the gas-phase). The latter is either hydrogenated into *cis*-product or desorbs and readsorbs on the opposite side of its double bond, forming O′. The latter is hydrogenated into *trans* product. Possible *cis*–*trans* isomerization is also taken into account.

The formation of *trans*-1,2-DMCH is believed to take place via roll over mechanism.



The derivation of the kinetic equations for the gas-phase hydrogenation of the aromatic ring was presented previously [6], where several cases were considered, including both competitive and non-competitive adsorption of the two reactants, dissociative and non-dissociative hydrogen adsorption as well as the possibility of several slow several reaction steps. For competitive adsorption, it was also taken into account, that hydrogen and the organic compounds can occupy different number of surface sites. The detailed kinetic modeling for *o*-xylene hydrogenation over Pt based on several variants of the reaction mechanism is outside of the scope of the present study and will be reported separately. However, it seems appropriate to demonstrate the link between the simplified power-law equation and kinetic equations derived from the detailed reaction mechanism.

For instance in case of competitive adsorption and equal number of sites for all adsorbed species the rate expression takes a form

$$r = \frac{k_1 k_2 k_3 K_X K_H^3 p_X p_{H_2}^3 / k_{-1} k_{-2}}{(a' K_X p_X + K_H^{1/j} p_{H_2}^{1/j} + 1)^{j+1} (1 + k_3 K_H p_{H_2}/k_{-2} + k_2 k_3 (K_H p_{H_2})^2 / k_{-1} k_{-2})} \quad (6)$$

with

$$a' = \frac{1 + (k_1/k_{-1} + k_3/k_{-2}) K_H p_H + (k_1 k_2/k_{-1} k_{-2} + k_1 k_3/k_{-1} k_{-2} + k_2 k_3/k_{-1} k_{-2}) K_H^2 p_H^2}{1 + (k_3/k_{-2}) K_H p_H + (k_2 k_3/k_{-1} k_{-2}) K_H^2 p_H^2} \quad (7)$$

For some values of parameters, Eq. (6) can be easily approximated to Eq. (5).

5. Conclusions

Gas-phase hydrogenation of *o*-xylene to *cis*- and *trans*-DMCH was studied in a differential microreactor at atmospheric pressure and 430–520 K over a Pt/γ-Al_2O_3 catalyst. Catalyst deactivated significantly with the deactivation rate being dependent of the conditions in the reactor.

A rate maximum for the production of the saturated compounds was observed at about 460 K. Reaction orders were close to zero for *o*-xylene, while hydrogen reaction order increases as a function of the temperature and ranged from 1.5 (430 K) to 3.0 (520 K).

The stereochemical distribution (*cis*/*trans* ratio) is dependent on the temperature as well as hydrogen pressure. The results were in line with previously reported results on xylene hydrogenation on Ni/γ-Al_2O_3 catalyst.

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