

Kinetics and stereoselectivity of *o*-xylene hydrogenation over Pd/Al₂O₃

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Abstract

Gas-phase hydrogenation of *o*-xylene was investigated over 1 wt.% Pd/alumina catalyst at 430–520 K. The catalyst was characterised by H₂-temperature programmed desorption (TPD), *o*-xylene-TPD, H₂-chemisorption, scanning electron microscope (SEM)/energy dispersive X-ray analyser (EDXA) and X-ray photoelectron spectroscopy (XPS). A reversible maximum in the *o*-xylene hydrogenation activity versus temperature was observed which owes to decreased surface aromatic concentration as indicated by *o*-xylene-TPD experiments. The reaction orders with respect to *o*-xylene were slightly negative (ca. –0.3) in the temperature range investigated, whereas orders with respect to hydrogen increased by temperature from 1.3 (at 440 K) to 2.5 (at 520 K). The catalyst exhibited a higher selectivity towards the formation of the *trans*-isomer of 1,2-dimethylcyclohexane. The product stereoselectivity was found to depend on the operation temperature and reactant concentrations. Concurrent dehydrogenation and configurational isomerisation of the product took place at considerable rates at the temperatures investigated. A reaction mechanism which involves the dehydrogenation and isomerisation reactions is proposed.

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1. Introduction

Hydrogenation of aromatics is used in oil refineries and petrochemical industries to increase the quality of the middle distillates in terms of cetane number and to lower the amount of carcinogenic aromatic compounds in fuels and solvents. Different model reactants have been chosen to understand the kinet-

ics of aromatics hydrogenation. The rate of aromatic hydrogenation is strongly affected by steric factors induced by the substitution of alkyl groups to the aromatic ring and is reported to decrease with increased length of the substituent (benzene > toluene > ethylbenzene > cumene) as well as increased number of substituents (benzene ≫ toluene ~ xylenes > mesitylene) [1–19]. The kinetics of gas-phase catalytic hydrogenation of xylenes has been investigated over supported Pd [3,10–12], Ni [13–19], Ru [11,20] and Pt [21–24] catalysts. The relative position of the substituents has a significant effect on the reaction

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rate, with *para*-position being the most reactive and the *ortho*-position the least one (*p*-xylene > *m*-xylene > *o*-xylene).

Similarly to benzene and toluene hydrogenation, a reversible temperature dependency of the activity maximum in xylene hydrogenation is observed [13–19,22]. The turnover frequencies in hydrogenation of xylenes are reported to increase by support acidity [3]. The nature of the catalyst and the operation conditions have a strong effect on the product stereoselectivity. Palladium is known to produce higher amounts of *trans*-1,2-dimethylcyclohexane [25,26] as compared to Ni, Rh and Pt [27,28]. The selectivity to the formation of *trans*-1,2-dimethylcyclohexane is reported to enhance by temperature, metal dispersion and the acidity of the support [10].

Although, there are several studies on gas-phase hydrogenation of xylenes over supported palladium catalysts addressing the issues of kinetics and stereoselectivity [10–12], the impact of dehydrogenation and epimerisation reactions on the overall mechanism is not very well understood. Noble metals in general and palladium in particular are known to be active in dehydrogenation reactions [29–31]. Moreover, the configurational isomerisation (between *cis*- and *trans*-1,2-dimethylcyclohexane) should be considered. The present work addresses the kinetics and the product stereoselectivity of the gas-phase hydrogenation of *o*-xylene over Pd/alumina catalyst. The *cis*-to-*trans*-1,2-dimethylcyclohexane epimerisation and the dehydrogenation of the products are also investigated.

2. Experimental

2.1. Catalyst

The 1 wt.% Pd/alumina catalyst was prepared by impregnation of a γ -alumina support (LaRoche, Versal GL25), having a BET surface area of 249 m²/g, with solution of pre-acidified PdCl₂. The catalyst was washed with deionised water, dried and stored for its activity testing. The metal content of the catalyst was determined by direct current plasma technique (Spectraspan IIIA, Spectrometrics).

2.2. Catalyst characterisation

The metal dispersion and mean metal particle diameter was determined by hydrogen adsorption by using a sorptometer (Sorptomatic 1900, Carlo Erba Instruments). In order to minimise the H₂-absorption by palladium, the adsorption isotherms were obtained at 363 K and pressures of 0.13–13.3 bar. The amount of reversibly adsorbed hydrogen was determined by back-sorption method. Extrapolation of adsorption isotherms to zero pressure was used to determine the amount of irreversibly adsorbed hydrogen. Prior to the H₂-adsorption, the catalyst was reduced in situ under hydrogen flow at 673 K for 2 h. Dissociative adsorption of hydrogen was adopted and the catalyst metal particle size was determined by assuming spherical particle geometry.

The temperature programmed desorption (TPD) of hydrogen and *o*-xylene was carried out using a volumetric equipment (Auto Chem 2910, Micromeritics). Prior to the adsorption studies, the samples were reduced in situ at 673 K. For the H₂-TPD studies, the hydrogen adsorption was carried out at 363 K. Desorbed gases were identified and analysed by a quadruple mass spectrometer (Omnistar, Baltzer Instruments). In *o*-xylene-TPD experiments, the mass spectrometer was calibrated for the fragmentation compounds.

The surface and sub-surface composition of the catalyst was investigated by scanning electron microscope (SEM, Leica Cambridge, Stereoscan 360) equipped with energy dispersive X-ray analyser (EDXA) and X-ray photoelectron spectroscopy (XPS, Perkin-Elmer 5400).

2.3. Catalytic activity measurements

2.3.1. *o*-Xylene hydrogenation

The kinetics of *o*-xylene hydrogenation was studied in a continuous flow differential tube reactor at WHSV of 70 h⁻¹ and temperatures of 440–520 K in 10 K intervals at atmospheric pressure. The partial pressures of H₂ (AGA, 99.9999 vol.%) and *o*-xylene (Fluka, >99.5%) were varied between 0.248 and 0.621, 0.0621 and 0.125 bar, using argon (AGA, 99.9999 vol.%) as the make-up gas keeping a constant GHSV. The flows were controlled by means of mass flow controllers (Brooks). The catalyst temperature was measured by use of a K-type thermocouple co-axially inserted

into the catalyst bed. Liquid *o*-xylene was fed by a high performance liquid chromatography pump (2150 HPLC pump, LKB Bromma) to an evaporator (Bronkhorst) kept at 443 K and was further driven by argon. All the lines after the evaporator and the reactor were heated. The reaction products were analysed by a Varian GC equipped with a 60 m HP-1 column (cross-linked methyl siloxane) and an FI-detector. Separation was carried out isothermally (373 K) and the products were further identified by GC-MS (HP 6890–5973 Instrument). Prior to the experiment, the dried catalyst (125–150 μm particles, ca. 100 mg) was reduced in situ under H_2 flow at 673 K for 2 h followed by cooling to the reaction temperature at which point the reactants were introduced to the catalyst. Additional experiments (i.e. the effect of flow and particle sizes) were carried out to ensure that the kinetics is measured in the absence of external and internal diffusion limitations. The conversions were kept below 10%.

2.3.2. 1,2-Dimethylcyclohexane (1,2-DMCH) configurational isomerisation and dehydrogenation

The isomerisation and dehydrogenation of 1,2-DMCH was studied in the same experimental set-up described for *o*-xylene hydrogenation in the temperature range of 470–520 K and partial pressures of *cis*- and *trans*-1,2-DMCH and hydrogen of 0.77×10^{-3} , 0.14×10^{-3} and 0.248–0.621 bar; respectively. Prior to the experiment, the catalyst (ca. 100 mg) was reduced at 673 K for 2 h under hydrogen flow, cooled down to the reaction temperature at which point the reactants were introduced. *N*-Heptane was used for dilution of the feed 1,2-DMCH. The *cis*- and *trans*-isomer content of the feed 1,2-DMCH (Fluka >99.5%) was 84 and 15.3 mol%, respectively.

3. Results and discussion

3.1. Catalyst characterisation

The metallic dispersion determined by H_2 -adsorption was found to be 93% with an average palladium particle diameter of 1.2 nm (assuming a spherical geometry). The SEM/EDX and XPS analyses of the surface and sub-surface composition of the catalyst are given in Tables 1 and 2. The SEM/EDX analy-

Table 1
SEM/EDX analysis of the 1 wt.% Pd/alumina catalyst

Catalyst	Cl/Pd	Cl/Al
Fresh	1.62	0.011
Reduced at 673 K	1.53	0.009
Alumina support	–	0.004

sis indicated the presence of chlorine on the catalyst surface. Reduction of the catalyst at 673 K resulted in the removal of a ca. 18% of the initial chlorine. The retention of chlorine by alumina has been reported previously [32,33]. It should be mentioned that traces of chlorine are present on the γ -alumina support (Table 1).

The existence of surface chlorine before and after reduction was further confirmed by XPS analysis (Table 2). The XPS data indicated a BE of 336.2 eV on the freshly dried sample, which corresponds to Pd^{2+} , most probably stabilised as PdCl_2 . This is in agreement with the observed Cl/Pd ratio of 1.62 (Table 1). Reduction of the catalyst lowered the Pd 3d_{5/2} BE value by 1.5 eV and metallic Pd was the dominant surface species. It appears that, Cl and Pd retain their co-ordination (from the precursor complex) on the fresh Pd/alumina catalyst. During the catalyst reduction, under the action of hydrogen, chlorine is removed from the Pd to the alumina carrier by exchange with the surface hydroxyl groups.

3.2. Hydrogenation of *o*-xylene

Hydrogenation of *o*-xylene took place readily at a temperature range investigated with *cis*- and *trans*-1,2-dimethylcyclohexane (1,2-DMCH) being the only products. A typical kinetic experiment is presented in Fig. 1. A minor time-on-stream catalyst deactivation

Table 2
XPS analysis of the 1 wt.% Pd/alumina catalyst

Catalyst	BE (eV)			Atomic ratio	
	Pd 3d _{5/2}	Al 2p	Cl 2p _{3/2}	Cl/Pd	Cl/Al
Fresh	336.2	73.9	198.3	1.6	0.012
Reduced at 673 K	334.7	74.1	198.5	1.3	0.0098
Support	–	73.9	197.8	–	0.003

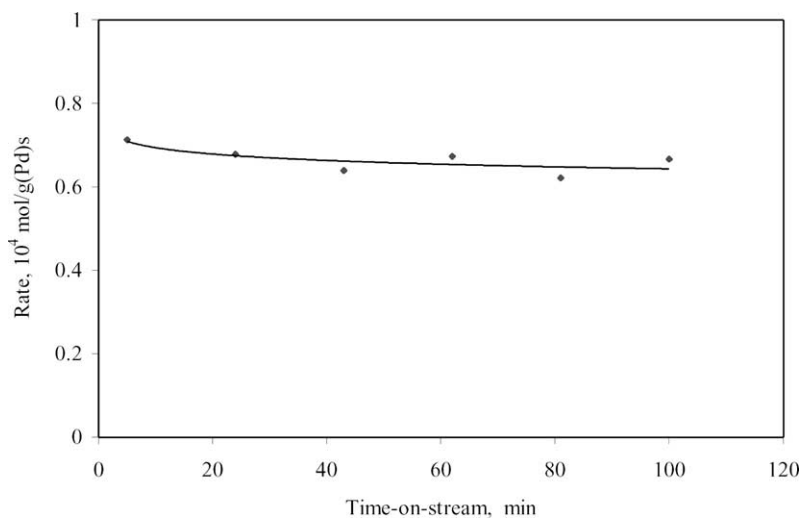


Fig. 1. Time-on-stream hydrogenation activity, 1 wt.% Pd/Al₂O₃, $T = 470$ K, $p_{\text{H}_2} = 0.621$ bar, $p_{o\text{-xylene}} = 0.0621$ bar.

took place, but the steady-state operation was obtained after ca. 20 min (Fig. 1). The catalyst deactivation was the same in the temperature range studied (Fig. 2). The deactivation is believed to be as a result of carbon deposition [34,35]. It should be mentioned that kinetic data reported hereafter are taken during the

steady-state operation. Hydrogen treatment of the used catalyst at 673 K for 2 h completely restored the initial catalyst activity.

A reversible temperature dependency of the activity maximum in xylene hydrogenation was observed at all hydrogen to *o*-xylene ratios investigated (Fig. 3).

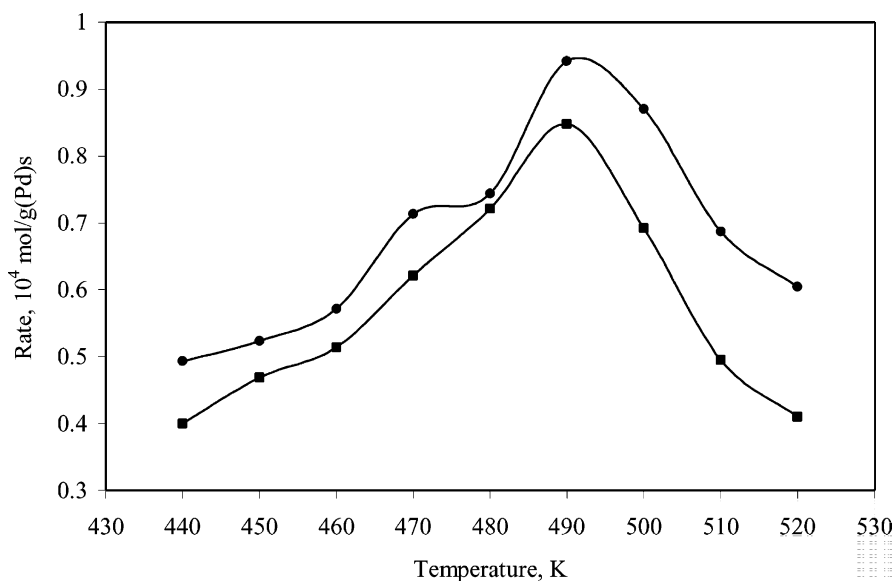


Fig. 2. The catalyst activity after 5 min (●) and 100 min (■) time-on-stream. $p_{\text{H}_2} = 0.62$ bar, $p_{o\text{-xylene}} = 0.062$ bar.

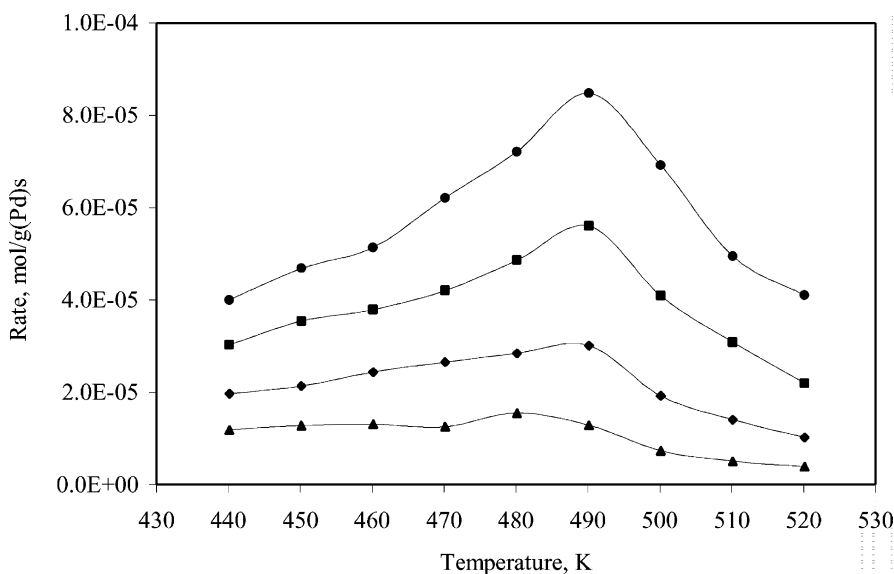


Fig. 3. Temperature dependency of the *o*-xylene hydrogenation at different hydrogen concentrations. $p_{o\text{-xylene}} = 0.062$ bar. (●) $p_{H_2} = 0.62$ bar; (■) $p_{H_2} = 0.49$ bar; (◆) $p_{H_2} = 0.36$ bar; (▲) $p_{H_2} = 0.24$ bar.

Such temperature dependencies of aromatics hydrogenation are commonly observed [3,4,8,9,13–19,22]. The thermodynamic calculation for the gas composition at the operation temperatures used confirmed that the experimental data are obtained in the lower region very far from the thermodynamic equilibrium, therefore, the decrease in the hydrogenation rate above 490 K can be solely attributed to the hydrogenation kinetics.

In order to investigate the effect of surface coverages of reactants on the formation of T_{\max} (temperature of maximum catalyst activity), hydrogen and *o*-xylene-TPD experiments were carried out over pre-reduced (673 K, 2 h in H_2 flow) catalyst. The H_2 -TPD pattern indicated a high surface coverage of hydrogen in the temperature range investigated with peak maxima at 423 and 673 K. The *o*-xylene-TPD pattern is presented in Fig. 4. *o*-Xylene desorption pattern was observed in the temperature range of 370–520 K with a maximum at around 450 K. The hydrogenolysis products, toluene and benzene, were observed at the same temperature range following the same desorption pattern as *o*-xylene. Ethene (mass 28), which is formed from the re-combination of the methyl groups, was also detected. At temperatures exceed-

ing 573 K increased cracking (i.e. ethene, methane and hydrogen evolution) took place. The hydrogenation activity pattern follows well the *o*-xylene-TPD pattern (Figs. 3 and 4) and is a clear indication of decreased surface concentration of aromatic at higher temperature, which ultimately results in decreased hydrogenation rate and formation of T_{\max} .

The reaction orders with respect to hydrogen and *o*-xylene were determined in the temperature and reactant partial pressures investigated. The reaction orders with respect to hydrogen (Fig. 5) increased monotonically by increased operation temperatures from 1.3 (at 440 K) to 2.6 (at 520 K). Such high reaction orders with respect to hydrogen have been previously reported for xylene hydrogenation over platinum and nickel catalysts [13–17,33]. The reaction orders with respect to *o*-xylene were ca. -0.3 and were not affected by the temperature.

Conventionally, the addition of first hydrogen pair is assumed to be the rate-determining step in aromatic hydrogenation. The *o*-xylene hydrogenation experiments indicated an increased reaction order with respect to hydrogen by increased operation temperature (Fig. 5). Mirodatos et al. [36] in their isotopic transient study have demonstrated that at low temperatures and

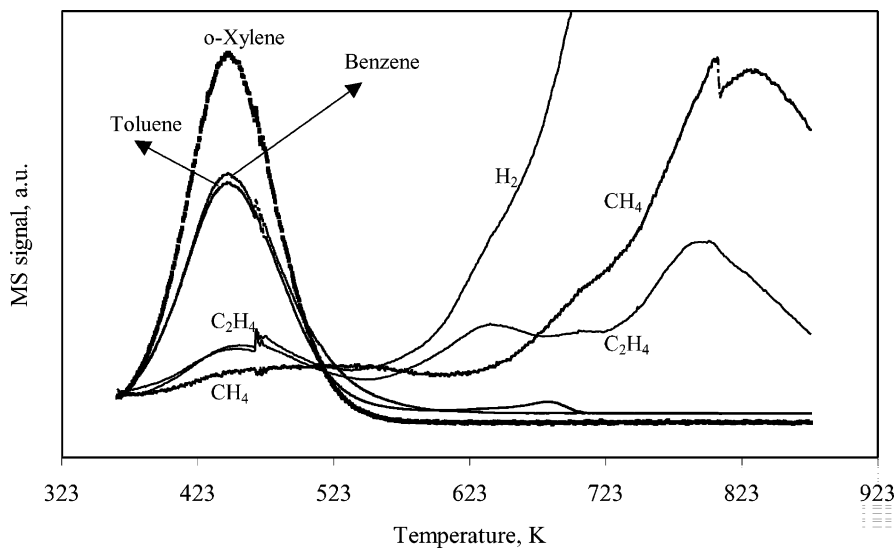


Fig. 4. TPD of *o*-xylene over 1 wt.% Pd/Al₂O₃ catalyst.

pressures, hydrogen is added pair-wise to benzene over nickel catalyst. If a pair-wise addition of the first hydrogen atoms is therefore considered, the overall reaction order with respect to hydrogen should equal the number of slow, i.e. rate-determining steps, and

equilibrium surface reaction steps. In such a case, the reaction order with respect to hydrogen should not exceed one. However, high reaction orders with respect to hydrogen are often observed [4,5,13–17,33,37,38] and this could imply that all of three hydrogen addition

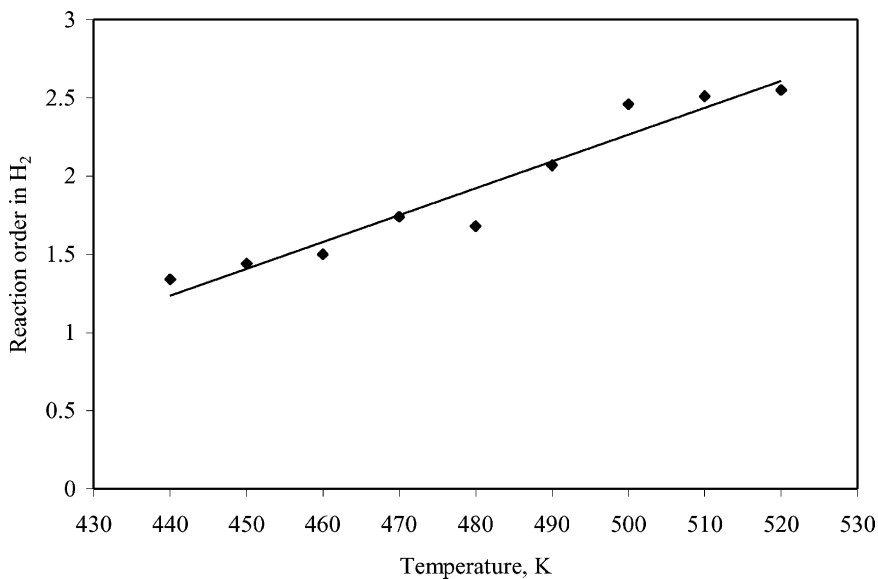


Fig. 5. Temperature dependency of the reaction orders with respect to hydrogen, $p_{o\text{-xylene}} = 0.062$ bar.

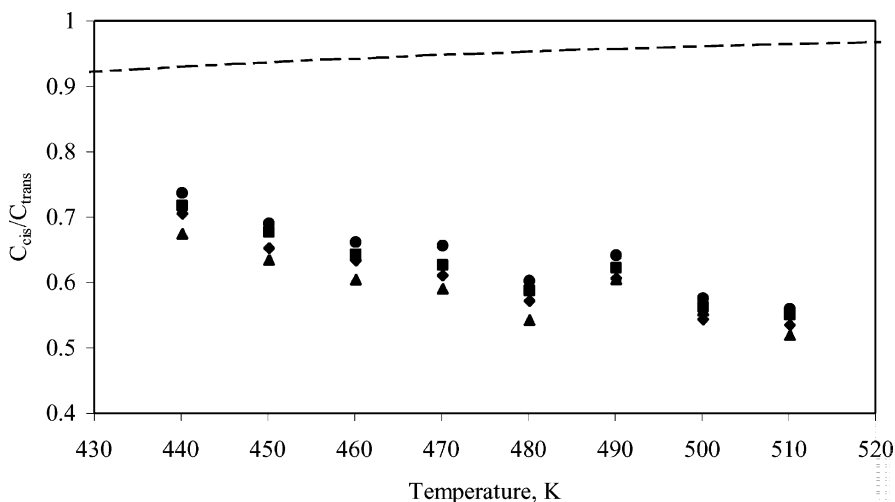


Fig. 6. The *cis-to-trans* ratio as a function of reaction temperature, $p_{o\text{-xylene}} = 0.062$ bar. (●) $p_{\text{H}_2} = 0.62$ bar; (■) $p_{\text{H}_2} = 0.49$ bar; (◆) $p_{\text{H}_2} = 0.36$ bar; (▲) $p_{\text{H}_2} = 0.24$ bar. Broken line: thermodynamic equilibrium.

steps are determining the overall rate. Smeds et al. [13,14], in line with the aromaticity principle proposed by Temkin [39], suggested a mechanistical scheme in which the aromatic character of the substrate is preserved during the first two hydrogen addition steps, and consequently avoiding the thermodynamically forbidden cyclohexadiene surface intermediate. In such way the reaction orders with respect to hydrogen of up to three could be explained by assuming that all three hydrogen addition steps contribute to the rate. Alternatively, Vannice and co-workers [9,40] in their study of hydrogenation of benzene and toluene have proposed a concurrent surface dehydrogenation reaction involving the aromatic reactant, resulting in the formation of a hydrogen-deficient surface species.

3.2.1. Stereoselectivity

The results indicated an increased selectivity to the formation of thermodynamically favoured *trans*-1,2-DMCH by increased operation temperature. The selectivity to the formation of *trans*-isomer, on the other hand is decreased by increased hydrogen partial pressure (Fig. 6). The changes in the *o*-xylene concentration did not affect the *cis-to-trans* ratio to a great extent. It should be pointed out that the initial catalyst deactivation did not alter the stereoselectivities either.

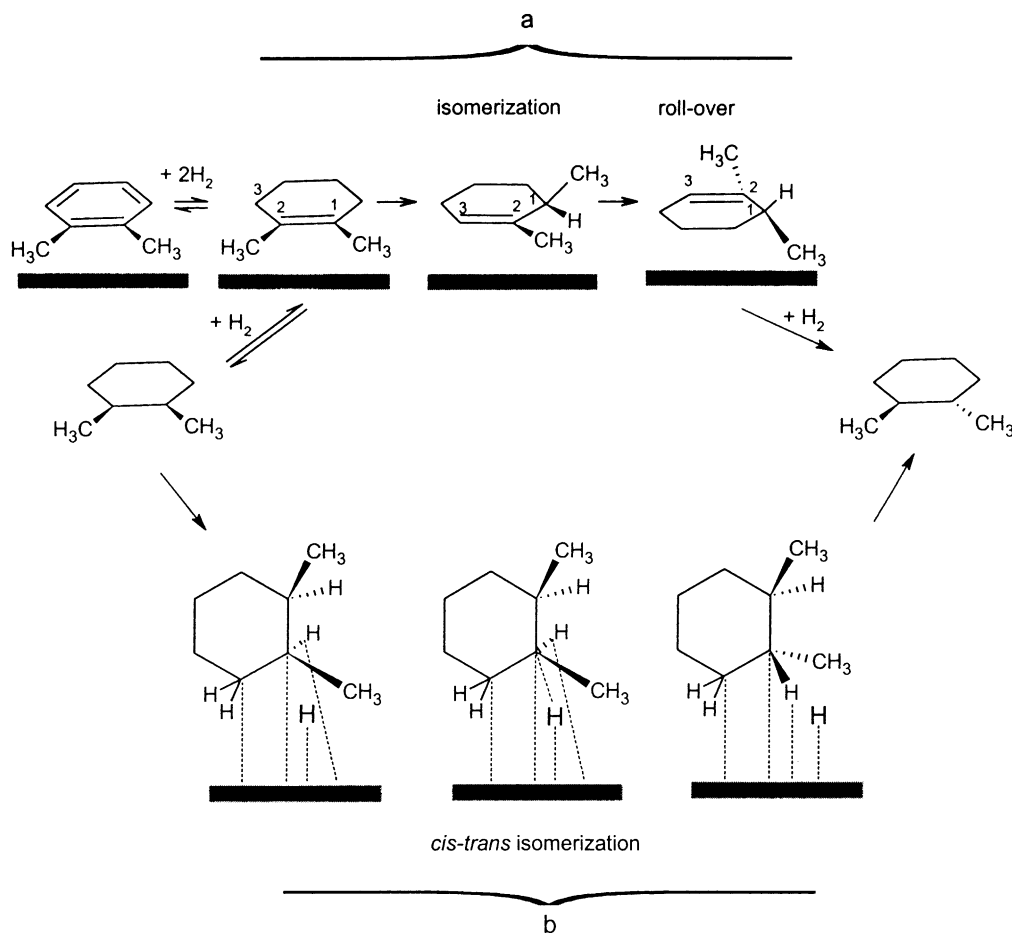
As mentioned, in the present study a higher selectivity towards the formation of the *trans*-isomer was

observed. However, previously [33] we have demonstrated a higher selectivity toward the formation of *cis*-isomer over alumina-supported platinum catalysts. There, the same observations, i.e. decreased selectivity to the formation of *trans*-isomer by increased hydrogen concentration and increased selectivity to *trans*-isomer by increased operation temperature was observed. Such observations are also in line with those reported for *o*-xylene hydrogenation over supported Pd and Ni and Pt catalysts [10,14–16,23]. The observed stereoselectivities are purely kinetic effect and can be influenced by the nature of the active metal and the precursor used in catalyst preparation, e.g. the residual chlorine from the catalyst precursor on the alumina support strongly affects the stereoselectivities [35]. Vinięgra et al. [10] demonstrated that the change in the electron density of palladium caused by the presence of electron donor compounds such as pyridine also increases the selectivity to the formation of the *cis*-isomer.

o-Xylene is known to adsorb with aromatic ring parallel to the surface [41,42]. In order to relief the steric repulsion, the two methyl groups should be oriented away from the surface. Under such conditions the formation of the thermodynamically less stable *cis*-isomer is obtained, i.e. the kinetic control prevails. Our data indicated a decreased *cis-to-trans* ratio from 0.75 (at 420 K) to 0.55 (at 520 K). The formation

of *trans*-isomer and its increased formation rate at higher temperatures has been discussed in a variety of ways. Siegel et al. [43] suggested for liquid-phase hydrogenation reactions that the cycloalkenes formed from the *cis* addition of four hydrogen atoms to the xylene molecule are desorbed from the surface and re-adsorbed, followed by hydrogenation of the double bond to form the *trans*-isomer. However, the *cis*-to-*trans* ratio of unity and lower (as in the present study) is often observed and this would suggest that at least half of the tetrahydrogenated molecules should desorb and re-adsorb. Keane [16] and Keane and Patterson [18] explained the phenomenon as a decrease in the surface concentration of aromatics at higher temperatures and relieve of the geometrical constrain. The

authors proposed that the weakening of the surface interaction and decreased crowding with increased temperature allows the re-arrangement of atoms not directly involved in the binding process and consequently increase in the proportion of *trans*-product. The increased selectivity to *trans*-isomer as a function of temperature and increased metal dispersion has intensively been explained by roll-over mechanism proposed by Inuone et al. [44], where the model well explained the exchange of hydrogen atoms on both sides of cyclopentane molecule (over Pd catalysts). The model has been applied to explain the stereoselectivity in *o*-xylene hydrogenation [10–15,21–24] as the last double bond to be hydrogenated isomerises before the roll-over step. Further hydrogen



Scheme 1. *o*-Xylene hydrogenation mechanism on Pd.

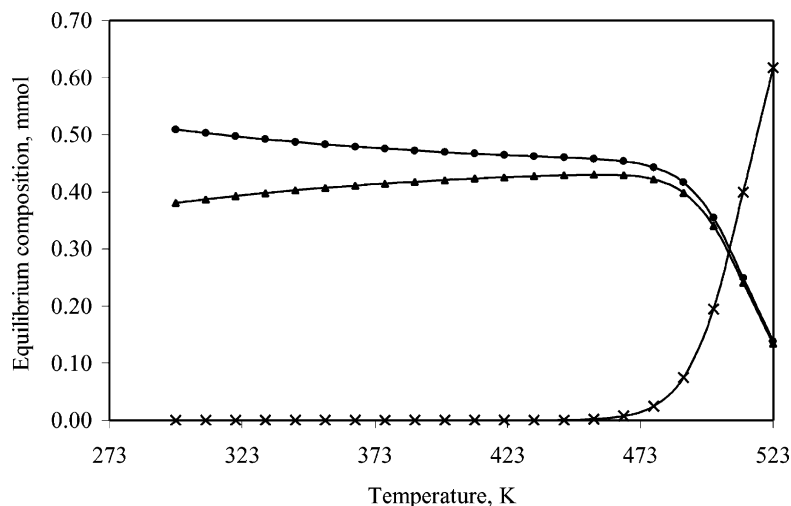


Fig. 7. Thermodynamic equilibrium for epimerisation and dehydrogenation reactions. Conditions: $p_{\text{H}_2} = 0.62$ bar, $p_{\text{cis-1,2-DMCH}} = 0.77 \times 10^{-3}$ bar, $p_{\text{trans-1,2-DMCH}} = 0.14 \times 10^{-3}$ bar. (\blacktriangle) *cis*-1,2-DMCH; (\bullet) *trans*-1,2-DMCH; (\times) *o*-xylene.

addition results in the formation of *trans*-isomer. The roll-over mechanism is presented in Scheme 1, where 1,2-dimethylcyclohexene (1,2-DMCHe) isomerises to 2,3-dimethylcyclohexene (2,3-DMCHe) and the latter rolls over and provides the condition for the formation of *trans*-isomer by hydrogenation of the double bond (Scheme 1). In this scheme one could also consider a desorption and re-adsorption of the 2,3-DMCHe from the other side of plane beside the roll over. The rate of formation of *trans*-isomer is therefore determined by the relative ratio of hydrogenation of 1,2-DMCHe and its isomerisation.

3.3. Dehydrogenation and epimerisation of 1,2-DMCH

The dehydrogenation of cyclohexane and cyclohexadiene over noble metals takes place rapidly at low temperature in the presence of hydrogen [45–49]. The reaction rate is reported to increase with an increased hydrogen-to-hydrocarbon ratio [46] and metal dispersion [50]. Thermodynamic calculations for dehydrogenation and epimerisation reactions under the conditions investigated were carried using HSC Chemistry[®] software (Outokumpu Ltd.) and the thermodynamic data for the compounds were taken from [51–53]. The calculation results are given in Fig. 7. The *cis*-to-*trans*-1,2-DMCH isomerisation is

favoured, whereas at temperatures exceeding 673 K, *o*-xylene formation is no longer restricted (Fig. 7). The present study indicates that the dehydrogenation and *cis*-to-*trans* isomerisation reactions are taking place in the temperature range and partial pressures investigated (Fig. 8). The presence of hydrogen was found to be essential for dehydrogenation and epimerisation, as when the hydrogen flow was replaced by argon the reactions immediately decreased. By re-introduction of hydrogen, the activity compared to the steady-state was partially restored (Fig. 9, Table 4). An analogous activity restoration has been reported for the configurational isomerisation of dimethylcyclohexane over an alumina-supported platinum catalyst [54]. As demonstrated in Table 4, the restoration of the activity is enhanced at elevated temperatures, which is the consequence of carbon deposit removal at higher temperatures.

The rate of *trans*-isomer formation was found to pass through a maximum at 480 K, close to the T_{max} in *o*-xylene hydrogenation (Fig. 8). The reaction orders with respect to hydrogen in *trans*-1,2-DMCH and *o*-xylene formation as well as *cis*-1,2-DMCH consumption were determined in the temperature range investigated and are given in Table 3. The rate of *trans*-isomer formation is increased by elevating the partial pressure of hydrogen, whereas at lower temperatures the dehydrogenation rate is strongly inhibited

by hydrogen (Fig. 8c and Table 3). The inhibition effect of hydrogen on the rate of *o*-xylene formation is decreased at higher temperatures. As shown in Fig. 8, at temperatures above 480 K the rate of *trans*-isomer

formation is declined and *cis*-1,2-DMCH is intensively dehydrogenated to *o*-xylene. The rate of dehydrogenation reactions is known to decrease by the presence of aromatics. At temperatures above 480 K desorption of

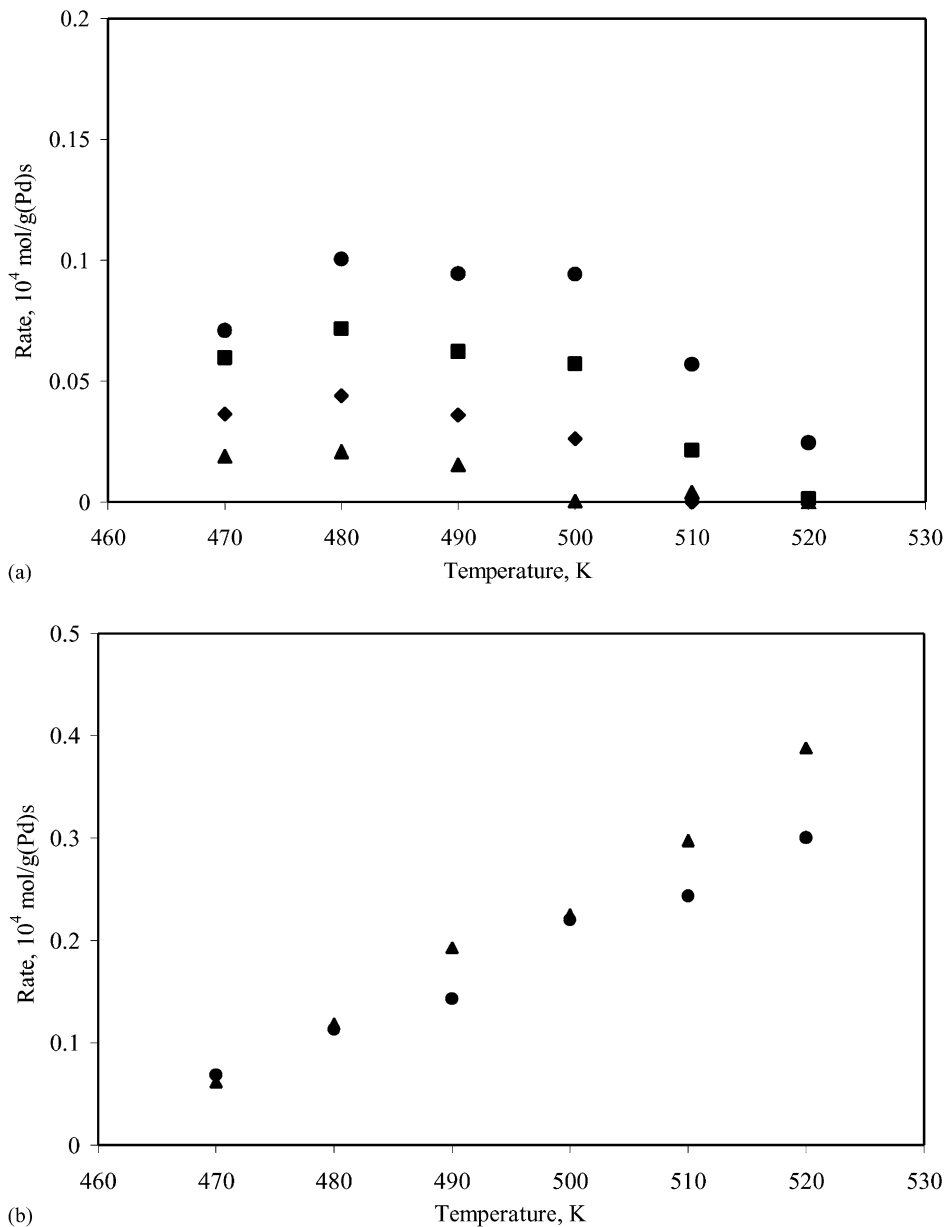


Fig. 8. Temperature dependency of dehydrogenation and epimerisation reactions: (a) formation of *trans*-isomer, (b) consumption of *cis*-isomer and (c) formation of *o*-xylene. (●) $p_{H_2} = 0.62$ bar; (■) $p_{H_2} = 0.49$ bar; (◆) $p_{H_2} = 0.36$ bar; (▲) $p_{H_2} = 0.24$ bar ($p_{cis-1,2-DMCH} = 0.77 \times 10^{-3}$ bar, $p_{trans-1,2-DMCH} = 0.14 \times 10^{-3}$ bar).

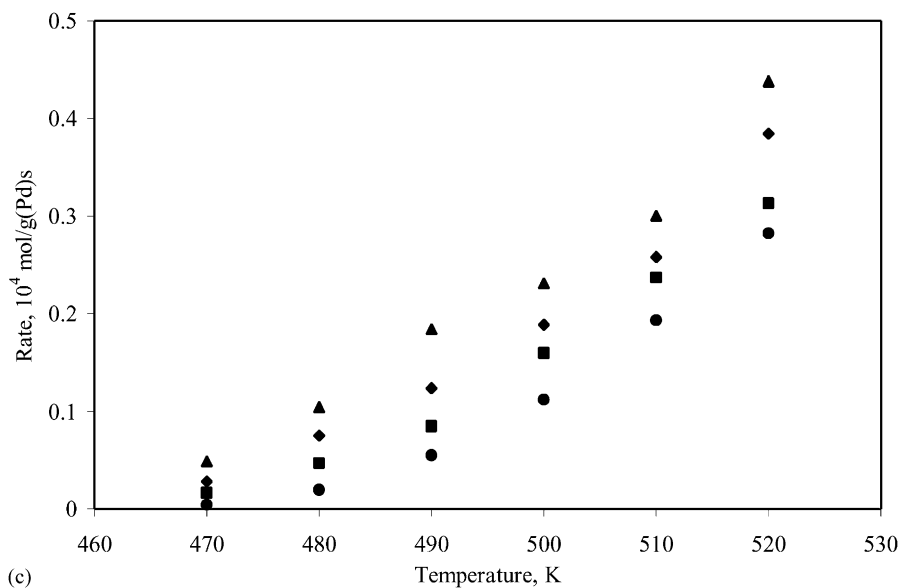


Fig. 8. (Continued).

formed *o*-xylene from the surface is intensified (see TPD pattern, Fig. 4) and hence increased rate of dehydrogenation is observed.

Cis and *trans* dialkyl substituted cyclohexanes can undergo inter-conversion on Group VIII metals. The

activity of the metals in the liquid-phase epimerisation of 1,2-DMCH is reported as: Rh > Ir > Pt > Pd ~ Ru > Ni [55]. The rate of epimerisation of alkyl cyclohexane over Pd is shown to depend on the dispersion and the structure sensitivity is depending on the

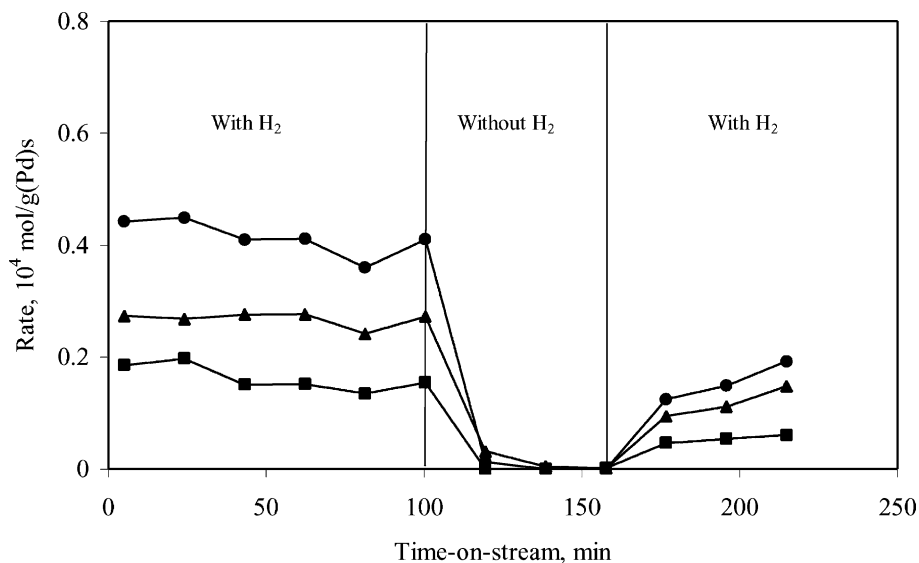


Fig. 9. Effect of hydrogen on dehydrogenation and epimerisation of 1,2-DMCH. Conditions: $T = 500$ K; $p_{H_2} = 0.62$ bar, $p_{cis-1,2-DMCH} = 1.84 \times 10^{-3}$ bar, $p_{trans-1,2-DMCH} = 0.33 \times 10^{-3}$ bar. (●) *cis*-isomer consumption, (■) *trans*-isomer formation and (▲) *o*-xylene formation.

Table 3
Reaction orders with respect to hydrogen for 1,2-DMCH epimerisation and dehydrogenation

Temperature (K)	Reaction order with respect to H ₂ in		
	<i>cis</i> -1,2-DMCH ^a	<i>trans</i> -1,2-DMCH ^b	<i>o</i> -Xylene ^b
470	^c	1.47	−2.45
480	^c	1.72	−1.71
490	−0.3	1.97	−1.29
500	−0.3	2.51	−0.74
510	−0.2	2.76	−0.45
520	−0.3	^c	−0.49

$p_{cis-1,2-DMCH} = 0.77 \times 10^{-3}$ bar, $p_{trans-1,2-DMCH} = 0.14 \times 10^{-3}$ bar and $p_{H_2} = 0.248$ – 0.621 bar.

^a Consumption.

^b Formation.

^c Low conversion levels.

temperature [56,57]. Both dissociative and associative mechanisms have been proposed for the epimerisation reactions. From the H–D exchange and epimerisation of alkyl cyclopentane investigations, Burwell and Schrage [58] proposed a dissociative mechanism according to which the cyclopentane ring is adsorbed by one face and is standing on the edge. The carbon atom in the edgewise-adsorbed state forms a penta-covalent state intermediate, which directs to the racemisation and epimerisation reactions. Shopov and Petrov [59] have proposed a mechanism for epimerisation of cyclohexane compounds, where the cyclic compound forms a σ -bonding to the surface, which leads to the formation of a common surface π -species from both isomers. This surface π -species reacts further with surface hydrogen forming the other stereoisomer.

The epimerisation of 1,2-DMCH can be ascribed by an associative S_N2 mechanism similar to that

presented by Bragin et al. [60] for epimerisation of cyclopentanes. The effect of hydrogen on the reaction rate is an indication of the role of hydrogen being not only for removal of carbon deposits (Table 4) but also for its participation in the reaction mechanism. We suggest the configurational isomerisation of 1,2-DMCH to proceed by the dissociative mechanism (S_N2) on the action of hydrogen, as presented in Scheme 1. According to this mechanism, *cis*-1,2-DMCH is adsorbed parallelly to the surface with hydrogen atoms forming H-bonding. Here, as was also confirmed from the experimental data, the presence of surface hydrogen is essential. In *cis*-to-*trans* isomerisation, according to S_N2 mechanism, hydrogen is an astoichiometric component. Here, one should expect a reaction order with respect to hydrogen in *trans*-isomer formation of close to unity. However, orders of up to 2.5 (Table 3) were observed and this might necessitate the inclusion of surface hydrogen-deficient species to the reaction mechanism similar to that reported by Chou and Vannice [40].

The rate of liquid-phase aromatisation of *cis*- and *trans*-1,2-DMCH is reported to be the same on platinum, whereas on palladium and nickel, the *trans*-isomer is converted substantially more slowly than the *cis*-isomer, which is believed to owe to the steric hindrance [61]. This is in agreement with our kinetic data as *cis*-isomer is predominantly aromatised at temperatures higher than 480 K (Fig. 9). The dehydrogenation of naphthanes over noble metals is presumed to follow a sequential dehydrogenation path. Cyclohexene has been identified on a Pt (1 1 1) surface from cyclohexane dehydrogenation [62]. The dehydrogenation of *cis*-1,2-DMCH can be represented by stepwise abstraction of hydrogen molecule (Scheme 1).

Table 4
Performance of Pd-catalyst in dehydrogenation and isomerisation of 1,2-DMCH

Temperature (K)	Rate at steady state ^a (10 ⁴ mol/g (Pd)s)			Regenerated rate ^b (10 ⁴ mol/g (Pd)s)		
	<i>r_{cis}</i>	<i>r_{trans}</i>	<i>r_{o-xylene}</i>	<i>r_{cis}</i>	<i>r_{trans}</i>	<i>r_{o-xylene}</i>
490	0.309	0.178	0.148	0.056	0.039	0.033
500	0.410	0.155	0.272	0.192	0.061	0.148
520	0.545	0.043	0.520	0.336	0.037	0.316

$T = 500$ K, $p_{H_2} = 0.622$ bar, $p_{cis-1,2-DMCH} = 1.84 \times 10^{-3}$ bar, $p_{trans-1,2-DMCH} = 0.33 \times 10^{-3}$ bar.

^a After 100 min.

^b Sixty minutes after re-introduction of H₂.

4. Conclusions

The gas-phase hydrogenation of *o*-xylene was studied in the temperature range of 440–520 K on the alumina-supported palladium catalyst. A reversible maximum in the hydrogenation rate by temperature was observed which owes to the decreased surface coverage of *o*-xylene as indicated from the *o*-xylene-TPD experiments. The overall reaction rate was found to increase with hydrogen concentration. The reaction orders with respect to *o*-xylene were slightly negative (−0.3) and did not change with temperature. The reaction orders with respect to hydrogen varied systematically between 1.3 (at 440 K) and 2.6 (at 520 K). The gas-phase hydrogenation of *o*-xylene over 1 wt.% Pd/alumina catalyst favours the formation of the thermodynamically more stable *trans*-isomer, the selectivity to the formation of which increases by increasing temperature. Concurrent to the *o*-xylene hydrogenation, dehydrogenation and epimerisation of the products takes place at considerable rates. The formation of *trans*-1,2-DMCH is believed mostly to follow the roll-over mechanism. A part of the *trans*-isomer is formed via epimerisation reaction following a S_N2 mechanism under direct participation of hydrogen (Scheme 1).

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