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Effect of isomerization on the performance of aromatic hydrogen storage systems possessing different condensation extents

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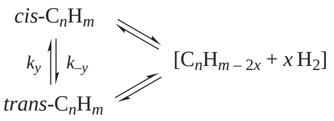
The influence of structural differences in *cis*- and *trans*-conformer molecules of *ortho*-, *meta*- and *para*-isomers of perhydroterphenyl and decalin on the hydrogen release in hydrogen storage systems was estimated for the Pt/C catalyst in a flow regime. The structural differences between the *cis*- and *trans*-conformers of perhydroterphenyl did not significantly affect the reactivity of its *ortho*-, *meta*- and *para*-isomers. In the case of decalin, the decrease in the volume of released hydrogen due to the conversion of its *cis*-isomer into the less active *trans*-form was clearly demonstrated.



$$\begin{tikzcd}
cis\text{-}C_nH_m \arrow[d, shift left, "k_{-y}"] \arrow[dr, shift left] & \\
trans\text{-}C_nH_m \arrow[u, shift left, "k_y"] \arrow[r, shift left] & {[C_nH_{m-2x} + x\,H_2]} \arrow[ul, shift left] \arrow[l, shift left]
\end{tikzcd}$$

A transition of global energy system based on the oil towards renewable sources requires the development of alternative concepts for energy storage. Hydrogen gas is a promising candidate to replace fossil fuels as the energy carrier featuring a high gravimetric storage density of 33 kWh kg^{-1}. However, the development of hydrogen-based energetics is limited by the insufficient availability and capacity of hydrogen storage systems that are also influenced by growing technology and safety demands.[1,2] The modern concept of hydrogen storage and transportation based on the application of organic compounds containing chemically bonded hydrogen and capable of storing and reversibly releasing up to 7.0–7.5 wt% of H_2 (hydrogen storage capacity) seems to be a breakthrough in the solution of key problems associated with hydrogen energetics. This method utilizes reversible cycles of the hydrogenation of diverse aromatic substrates (hydrogen storage stage) with the consequent dehydrogenation of their hydrogenated analogs (hydrogen release stage). It is extremely safe, since hydrogen is stored not in the gas state, but in the structure of organic hydride, whereas hydrogen is released on purpose at the moment of contact of the hydrogenated substrate with a catalyst in a controllable manner.[3] Such cyclic systems as benzene–cyclohexane and their derivatives are the most widely used for the hydrogen storage.[4–6] The presence of decalin in traditional fuels (diesel, kerosene, *etc*.) evokes an interest in the dehydrogenation of hydrocarbons with a higher degree of condensation, such as terphenyl.[7–14] The application of substrates with elevated boiling points exceeding the temperature of dehydrogenation reaction will result in a higher probability of suppression of the coke formation and catalyst deactivation. It has been already shown that the recycle of formed aromatic products does not impair the properties of initial fuel.[15]

A disadvantage of aromatic systems is the necessity to use relatively high dehydrogenation temperatures, while fuel cells for the automobile transport need low temperatures.[16–19] The application of Pt-containing catalysts allows one to decrease the activation energy for the dehydrogenation reaction of naphthenic molecules without cracking, hydrogenolysis, ring opening, or coke formation. The key in creating such the efficient systems is the proper design of carrier and the control of dispersion of metal nanoparticles and their interaction with the carrier surface. Quantum-chemical calculations revealed a relationship between a decrease in the dehydrogenation temperature and enthalpies of hydrogenation of the corresponding cyclic hydrocarbons.[10,11] The approximation to a required range of enthalpies correlates with the increased condensation extent of aromatic systems, but, unfortunately, only decalin is a liquid compound among the condensed systems, which limits the implementation of this approach.

According to thermodynamic calculations performed recently, the value of enthalpy change ΔH^0 at 300 K for the hydrogenation of naphthalene into *cis*- and *trans*-decalin is –63.35 and –66.15 kJ per 1 mole of H_2, respectively.[20,21] The calculated temperature for 95.24% conversion of decalin under the standard conditions for *cis*-isomer is 244 °C, while that for its *trans*-isomer is 273 °C. A simple comparison shows that, while the physicochemical characteristics of three terphenyl isomers and those of decalin are quite different, the enthalpy changes (ΔH^0 at 300 K) calculated for the hydrogenation of *m*- and *p*-terphenyl isomers (–65.73 and –66.15 kJ mol^{-1}) are virtually the same as that for *trans*-decalin and these substrates are nearly identical to each other from the thermodynamical viewpoint.

This work was devoted to the study of structural effect of condensed hydrogenated hydrocarbons derived from corresponding

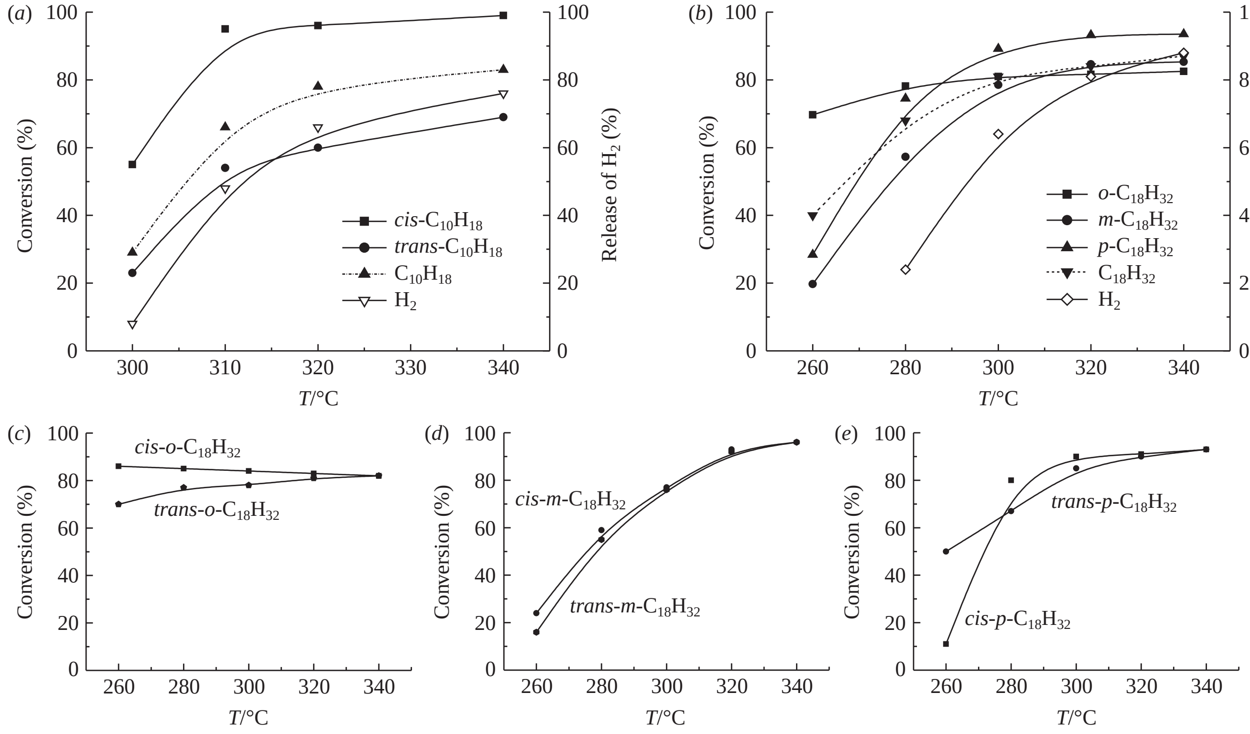


Figure 1 Temperature dependences of the conversion and extent of hydrogen release upon dehydrogenation of (*a*) decalin and (*b*)–(*e*) *ortho*-, *meta*- and *para*-isomers of perhydroterphenyl (V_L = 1 h^{-1} and *P* =1 atm).

aromatic substrates, in particular, *cis*- and *trans*-decalin isomers and *ortho*-, *meta*-, *para*-isomers of perhydroterphenyl on their ability to release hydrogen *via* dehydrogenation on a Pt/C (3 wt%) catalyst[24] in a flow reactor.[†]

The reversible reactions of hydrogenation of condensed aromatic hydrocarbons and dehydrogenation of the corresponding hydrogenated naphthenic molecules represent a multi-stage process described by the general scheme: $A–H_{2n} \leftrightarrow A + H_{2n}$. In addition to the hydrogen gas, the products of complete dehydrogenation are formed: naphthalene in the case of *cis*- and *trans*-decalin isomers and *ortho*-, *meta*- and *para*-isomers of terphenyl in the case of saturated perhydroterphenyl *ortho*-, *meta*- and *para*-isomers. Partially hydrogenated forms are the intermediate of side products and include tetralin ($C_{10}H_{14}$) and relevant partially hydrogenated derivatives of terphenyl containing two unsaturated rings ($C_{18}H_{20}$: *o*-, *m*- and *p*-diphenylcyclohexane and isomers of cyclohexylbiphenyl) or one unsaturated 6-membered ring ($C_{18}H_{26}$: isomers of dicyclohexylbenzene and cyclohexylphenylcyclohexane). If the process of dehydrogenation is carried out under severe conditions (elevated temperatures, reduced substrate space velocity, *etc*.), some trace amounts of products of cracking and hydrogenolysis (ring opening) can be observed, but the dehydrogenation rate is much higher as compared to the competitive reactions.

Figure 1 shows the temperature dependences of extent of the hydrogen evolution (as percentage of the theoretical value) and the conversion for the dehydrogenation of *cis*- and *trans*-decalin isomers, and *ortho*-, *meta*- and *para*-isomers of perhydroterphenyl.[‡]

The comparison of experimental curves shows that the conversions for the dehydrogenation of substrates in the *cis*-conformation exceed those for more rigid *trans*-conformation. Noteworthy, the ratios between the *cis*- and *trans*-forms for each substrate were different. In the cases of *cis*- and *trans*-isomers of decalin [Figure 1(*a*), curves *1* and *2*)] and perhydro-*m*-terphenyl, the conversions simultaneously increase with the temperature rise. However, while the curves for *cis*- and *trans*-isomers of perhydro-*m*-terphenyl virtually coincide with each other [Figure 1(*d*)], the difference between the *cis*- and *trans*-decalin is quite significant for the entire temperature range. In the case of *ortho*- and *para*-isomers of perhydroterphenyl, the dependences are more complicated. For perhydro-*o*-terphenyl [Figure 1(*c*)], an increase in the conversion of *trans*-isomer in the chosen temperature interval was observed as compared to the practically constant conversion of *cis*-isomer. In the case of perhydro-*p*-terphenyl [Figure 1(*e*)], the conversion of *cis*-isomer at low temperatures was significantly lower than that of *trans*-isomer, although after reaching 280 °C, the conversions were comparable within the experimental error.

[†] Decalin (98%, Acros Organics) contained 61% of *trans*-$C_{10}H_{18}$ (bp 185.5 °C) and 39% of *cis*-$C_{10}H_{18}$ (bp 194.6 °C). A mixture of three perhydroterphenyl isomers with the composition of *o*-$C_{18}H_{32}$ (12.17 wt%), *m*-$C_{18}H_{32}$ (58.65 wt.%), and *p*-$C_{18}H_{32}$ (26.27 wt%) was used to evaluate the behaviour of different isomers under the identical dehydrogenation conditions. This mixture was prepared by the hydrogenation of a commercial mixture of terphenyl isomers Santowax-R (10.61 wt% of *o*-$C_{18}H_{14}$, 56.99 wt% of *m*-$C_{18}H_{14}$, and 28.63 wt% of *p*-$C_{18}H_{14}$). The ratio between *cis*- and *trans*-isomers in the substrates for dehydrogenation and their melting points are shown in Table S1 (see Online Supplementary Materials).

[‡] The reaction products were analyzed using a Kristalux-4000M chromatograph equipped with a ZB-5 capillary column (ZEBRON, USA) and flame-ionization detector. The analysis was carried out in a temperature-programmed mode in the range of 70–220 °C at the heating rate of 6 K min^{-1}. Detailed identification of semi-hydrogenated and side products of perhydro-*m*-terphenyl dehydrogenation was performed using a FOCUS DSQ II chromatomass spectrometer equipped with a TR-5ms capillary column. The purity of generated hydrogen in the course of dehydrogenation was controlled by the gas chromatography using a thermal conductivity detector and a Porapack Q packed column.

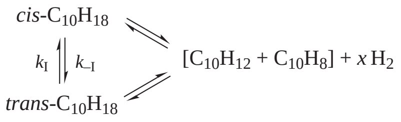
The conversion of substrates in the hydrogenation and dehydrogenation (*C*) was calculated *via* the formula: $C = (c^0 - c)/c^0 \times 100\%$, where c^0 and *c* are the initial and final concentrations of the converted substrate, respectively. The selectivity (*S*) was calculated using the formula: $S(i) = \sum c(i) / \sum c(k) \times 100\%$, wherein $\sum c(i)$ and $\sum c(k)$ are the sums of the concentrations of a group of products and all the products, respectively.

Note that the temperature dependence of total conversion of the *cis*- and *trans*-forms of perhydro-*m*-terphenyl [Figure 1(*a*), curve *2*] in the composition of studied mixture was lower than the total conversions of the *ortho*- and *para*-isomers.

The amount of evolved hydrogen during the *cis*- and *trans*-decalin dehydrogenation was in a good correlation with the overall conversion [Figure 1(*a*), curves *3* and *4*], while in the case of perhydroterphenyl isomers this dependence was not so clear [Figure 1(*b*), curves *4* and *5*]. The overall amount of released hydrogen upon dehydrogenation of mixture of perhydroterphenyl isomers was significantly larger as compared to decalin in spite of the close theoretical values for the hydrogen storage capacity (7.26 and 7.25 wt%, respectively). Therefore, the processes occurring during dehydrogenation should be considered in some more details. It should also be noted that the high purity of released hydrogen was established by the gas chromatography method, *e.g*., the total amount of impurities in hydrogen obtained in the case of perhydro-*m*-terphenyl dehydrogenation was not exceeding 0.03%.

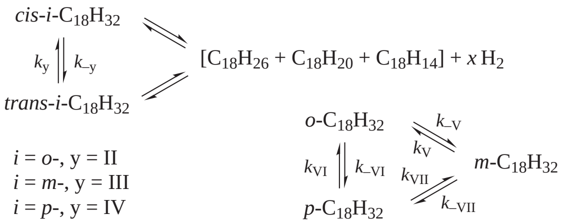
The variations in concentrations of the *cis*- and *trans*-decalin, as well as *ortho*-, *meta*- and *para*-isomers of perhydroterphenyl, in the reaction mixture during the dehydrogenation of these substrates as a function of reaction temperature ($V_L = 1\ h^{-1}$, $P = 1$ atm) are shown in Figure S1 (see Online Supplementary Materials). The dymamics of decrease in the concentrations of partially dehydrogenated products during the dehydrogenation of perhydroterphenyl isomers is in agreement with the accumulation of final products. Analysis of the experimental data has revealed that the dehydrogenation occurs predominantly at the terminal cyclohexane rings with the formation of cyclohexylphenylcyclohexane and dicyclohexylbenzene. For the *ortho*-isomer, the ratio between all the intermediates is more uniform, including the products with a different location of saturated and unsaturated rings.

Taking into account quite a significant number of intermediate products in the dehydrogenation reaction, especially in the case of mixture of perhydroterphenyl isomers, the experimental data were analyzed using the KINET 0.8 software for mathematical simulations of kinetics of the complex reactions.[25] This approach allows one to operate simultaneously (*via* integration) with up to 20 elementary steps and up to 15 compounds participating/formed in the process. We used an optimized mechanism (Scheme 1) in order to model the kinetics of decalin dehydrogenation, where the reaction can proceed simultaneously *via* several routes: the interconversion of *cis*- and *trans*-decalin isomers ($cis\text{-}C_{10}H_{18} \leftrightarrow trans\text{-}C_{10}H_{18}$; $K_I = k_I/k_{-I}$), formation of tetraline as an intermediate and the final product from *trans*-decalin [$trans\text{-}C_{10}H_{18} \leftrightarrow \sum(C_{10}H_{12} + C_{10}H_8 + H_2)$] and from *cis*-decalin [$cis\text{-}C_{10}H_{18} \leftrightarrow \sum(C_{10}H_{12} + C_{10}H_8 + H_2)$].



Scheme 1

In the case of mixture of *ortho*-, *meta*- and *para*-isomers of perhydroterphenyl, the number of compounds participating in the process is considerably larger. Therefore, the calculated general model scheme was represented as follows: $cis\text{-}i\text{-}C_{18}H_{32} \leftrightarrow trans\text{-}i\text{-}C_{18}H_{32}$, $cis\text{-}i\text{-}C_{18}H_{32} \leftrightarrow \sum(i\text{-}C_{18}H_{26} + i\text{-}C_{18}H_{20} + i\text{-}C_{18}H_{14} + H_2)$, $trans\text{-}i\text{-}C_{18}H_{32} \leftrightarrow \sum(i\text{-}C_{18}H_{26} + i\text{-}C_{18}H_{20} + i\text{-}C_{18}H_{14} + H_2)$, where *i* = *ortho*-, *meta*- or *para*-isomers. The corresponding equilibrium constants of *cis*–*trans* transformations (K_{eq}) for the each isomer and constants of their mutual isomerization were calculated as: $cis\text{-}o\text{-}C_{18}H_{32} \leftrightarrow trans\text{-}o\text{-}C_{18}H_{32}$ (K_{II}), $cis\text{-}m\text{-}C_{18}H_{32} \leftrightarrow trans\text{-}m\text{-}C_{18}H_{32}$ (K_{III}), $cis\text{-}p\text{-}C_{18}H_{32} \leftrightarrow trans\text{-}p\text{-}C_{18}H_{32}$ (K_{IV}), $o\text{-}C_{18}H_{32} \leftrightarrow m\text{-}C_{18}H_{32}$ (K_V), $o\text{-}C_{18}H_{32} \leftrightarrow p\text{-}C_{18}H_{32}$ (K_{IV}), $p\text{-}C_{18}H_{32} \leftrightarrow m\text{-}C_{18}H_{32}$ (K_{VII}). The rate constants of direct and reverse reactions (I–VII) were determined for isothermal conditions. The total concentrations of *cis*- and *trans*- isomers of *o*-, *m*- and *p*-perhydroterphenyl were used for the calculation of constants K_V–K_{VII}. The kinetic routes of possible interconversions are summarized in Scheme 2.



Scheme 2

The equilibrium constants of elementary steps for the interconversion of *cis*- and *trans*-decalin isomers and *ortho*-, *meta*- and *para*-isomers of perhydroterphenyl (I–VII) during the dehydrogenation in the temperature range of T = 280–340 °C have been estimated using the experimental data and are given in Table S2. The *trans*-decalin molecule is formed by two cyclohexane rings occupying the same plane, whereas two hydrogen atoms at the tertiary carbons are located at different sides of this plane. In *cis*-decalin, hydrogens are placed at the same side of the plane, whereas the rings form L-shaped structure.[26] The data (see Table S2) provide evidence for the advantages of the transformation of *cis*-decalin into a more stable *trans*-form (I) before the dehydrogenation reaction, which is in agreement with other reports.[10,11] Comparison of the experimental data [Figure 1(*a*)] suggests that the delay (a shift to higher temperatures) of conversion curve for *trans*-decalin can be also related to its additional formation from *cis*-decalin. The isomerization of *cis*-decalin into the less active trans-form leads to a decreased total rate of the dehydrogenation and finally causes a decrease in the amount of released hydrogen.

Among the three isomers (*ortho*-, *meta*-, and *para*-) of perhydroterphenyl, the structures of both *cis*- and *trans*-forms of perhydro-*p*-terphenyl are closest to the structure of decalin, since the *trans*-isomer forms a linear molecular chain, while the *cis*-isomer has a U-shaped structure. For the *cis*- and *trans*-conformers of *o*- and *m*-perhydroterphenyl, all the cyclohexane rings are aligned relatively close to the imaginary plane despite different conformations of the central ring.[23,27] The conversion of *cis*-isomer into the more stable *trans*-one (K_{II} and K_{III}) is favorable (see Table S2) for the *ortho*- and *meta*-isomers of perhydroterphenyl in the studied temperature range, similarly to the decalin isomers. For the *para*-isomer of perhydroterphenyl, the equilibrium constants (K_{IV}) are close to unity, although, the reverse transition of *trans*-isomer into the more active *cis*-conformation seems to prevail. Analysis of the experimental data (see Figure 1) suggests that, unlike the condensed molecule of decalin, the differences in the structures of the *cis*- and *trans*-forms of perhydroterphenyl do not exert any significant effect on the reactivity and hence the amounts of released hydrogen, especially at higher temperatures.

The reactions of isomerization do influence the behavior of *ortho*-, *meta*- and *para*-isomers of perhydroterphenyl.[22,28] The values of equilibrium constants (see Table S2) for the mutual interconversion of *o*-, *m*- and *p*-perhydroterphenyl (K_V–K_{VII}) at temperatures above 300 °C, *i.e.* in the region of high conversions, are rather significant to be neglected. The *o*-perhydroterphenyl is the least stable isomer, while the *meta*-isomer is most stable towards the isomerization, which agrees with the thermodynamic calculations of enthalpies of formation and enthalpies of isomerization of the corresponding *ortho*-, *meta*- and *para*-isomers of terphenyl.[29,30] Comparison of the calculated values of K_V–K_{VII} with the acquired data on hydrogen release (see Figure 1) demonstrates, however, that the processes of mutual interconversion (isomerization) in the course of dehydrogenation occur *via* the pathways including the formation of compounds that can be dehydrogenated with a higher rate. But the processes of isomerizations do not exert impact on formation products of cracking and deactivation of catalyst. Thus, the resultant effect on the hydrogen release in the case of perhydroterphenyl is not so significant as in the case of decalin dehydrogenation.

In conclusion, this work revealed the influence of structural peculiarities of *cis*- and *trans*-conformers of decalin and *ortho*-, *meta*- and *para*-isomers of perhydroterphenyl on the dehydrogenation reaction, *i.e*. the comparison of structures bearing the condensed and linearly aligned C_6 rings (the first and latter compounds, respectively). The transformation of *cis*-decalin into the less active *trans*-isomer suppresses the overall reaction rate. For bulkier molecules of *o*-, *m*- and *p*-perhydroterphenyl, the different pathways of mutual isomerization have been observed. The structural distinctions between its *cis*- and *trans*-conformers do not exhibit a significant effect on the reactivity and, correspondingly, on the amounts of released hydrogen, especially in the region of higher temperatures.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.01.007.

References

1 S. Satyapal, J. Petrovic, C. Read, G. Thomas and G. Ordaz, *Catal. Today*, 2007, **120**, 246.
2 H. L. Hellman and R. van den Hoed, *Int. J. Hydrogen Energy*, 2007, **32**, 305.
3 M. Taube, D. W. T. Rippin, D. L. Cresswell and W. Knecht, *Int. J. Hydrogen Energy*, 1983, **8**, 213.
4 A. A. Shukla, P. V. Gosavi, J. V. Pande, V. P. Kumar, K. V. R. Chary and R. B. Biniwale, *Int. J. Hydrogen Energy*, 2010, **35**, 4020.
5 N. Kariya, A. Fukuoka and M. Ichikawa, *Appl. Catal., A*, 2002, **233**, 91.
6 G. Maria, A. Marin, C. Wyss, S. Muller and E. Newson, *Chem. Eng. Sci*., 1996, **51**, 2891.
7 D. Sebastián, E. G. Bordejé, L. Calvillo, M. J. Lázaro and R. Moliner, *Int. J. Hydrogen Energy*, 2008, **33**, 1329.
8 S. Hodoshima, S. Takaiwa, A. Shono, K. Satoh and Y. Saito, *Appl. Catal., A*, 2005, **283**, 235.
9 S. Hodoshima, H. Arai, S. Takaiwa and Y. Saito, *Int. J. Hydrogen Energy*, 2003, **28**, 1255.
10 B. Wang, D. W. Goodman and G. F. Froment, *J. Catal*., 2008, **253**, 229.
11 A. N. Kalenchuk, D. N. Smetneva, V. I. Bogdan and L. M. Kustov, *Russ. Chem. Bull., Int. Ed*., 2015, **64**, 2642 (*Izv. Akad. Nauk, Ser. Khim*., 2015, 2642).
12 N. Kariya, A. Fukuoka, T. Utagawa, M. Sakuramoto, Y. Goto and M. Ichikawa, *Appl. Catal., A*, 2003, **247**, 247.
13 L. M. Kustov, A. L. Tarasov, J. Sung and D. Yu. Godovsky, *Mendeleev Commun*., 2014, **24**, 1.
14 J. S. Sung, K. Y. Choo, T. H. Kim, A. L. Tarasov, O. P. Tkachenko and L. M. Kustov, *Int. J. Hydrogen Energy*, 2008, **33**, 2721.
15 C. Resini, C. Lucarelli, M. Taillades-Jacquin, K.-E. Liew, I. Gabellini, S. Albonetti, D. Wails, J. Rozière, A. Vaccari and D. Jones, *Int. J. Hydrogen Energy*, 2011, **36**, 5972.
16 E. Clot, O. Eisenstein and R. H. Crabtree, *Chem. Commun*., 2007, 2231.
17 M. Yang, Y. Dong, S. Fei, H. Ke and H. Cheng, *Int. J. Hydrogen Energy*, 2014, **39**, 18976.
18 D. Dean, B. Davis and P. G. Jessop, *New J. Chem*., 2011, **35**, 417.
19 M. Amende, C. Gleichweit, K. Werner, S. Schernich, W. Zhao, M. P. A. Lorenz, O. Höfert, C. Papp, M. Koch, P. Wasserscheid, M. Laurin, H.-P. Steinrück and J. Libuda, *ACS Catal*., 2014, **4**, 657.
20 G. P. Pez, A. R. Scott, A. C. Cooper and H. Cheng, *US Patent 7101530 B2*, 2005.
21 G. P. Pez, A. R. Scott, A. C. Cooper and H. Cheng, *US Patent 20040223907 A1*, 2003.
22 A. N. Kalenchuk, V. I. Bogdan, S. F. Dunaev and L. M. Kustov, *Fuel Process. Technol*., 2018, **169**, 94.
23 W. Brügel, E. Kuss, T. Pollmann and H. Stegemeyer, *J. Mol. Struct*., 1967, **1**, 61.
24 A. N. Kalenchuk, V. I. Bogdan, S. F. Dunaev and L. M. Kustov, *Int. J. Hydrogen Energy*, 2018, **43**, 6191.
25 A. V. Abramenkov, in *Praktikum po Fizicheskoi Khimii (Practical Works in Physical Chemistry)*, eds. V. V. Lunin and E. P. Ageev, Akademiya, Moscow, 2012 (in Russian).
26 E. L. Eliel, S. H. Wilen and M. P. Doyle, *Basic Organic Stereochemistry*, Willey-Interscience, New York, 2001.
27 K. Sasvari and L. Parkanyi, *Acta Crystallogr*., 1976, **B32**, 1059.
28 A. N. Kalenchuk, V. I. Bogdan, S. E. Bogorodskii and L. M. Kustov, *Kinet. Catal*., 2016, **57**, 219 (*Kinet. Katal*., 2016, **57**, 213).
29 M. A. V. Ribeiro da Silva, L. M. N. B. F. Santos, S. Spencer and L. M. Lima, *J. Chem. Thermodyn*., 2008, **40**, 375.
30 S. P. Verevkin, *J. Chem. Thermodyn*., 1999, **31**, 559.

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