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Reaction pathways and kinetics of the gas-phase oxidation of cyclohexane on NiO/γ-Al_2O_3 catalyst

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Abstract

A NiO/γ-Al_2O_3 catalyst with a nearly monolayer dispersion of active nickel oxide species on the carrier was synthesized and investigated for the selective oxidehydrogenation of cyclohexane to cyclohexene. Integral measurements were performed to determine the reaction network and products distribution and differential measurements for kinetic investigations. The kinetic study showed a mechanism change in the temperature range of 573–603 K. From 513 to 573 K the oxidation took place via electrophilic oxygen species and from 603 to 723 K with nucleophilic oxygen species. The reaction order of cyclohexane is 1.0 in the lower temperature range and 0.5 in the higher one.

Keywords: Cyclohexane oxidation; Oxidehydrogenation; Cyclohexene; NiO/γ-Al_2O_3 catalyst; Oxidation mechanism

1. Introduction

The activation and functionalization of paraffins is one of the world wide pursuit research directions with a high potential for the development of new catalytic process technologies. The oxidation of cyclohexane to cyclohexanol and cyclohexanone, the intermediates of a large palette of plastics, is performed industrially in the liquid phase by using homogeneous catalysts and air as an oxidant. This process has low yields, is operated at hard temperature and pressure conditions and requires high energy consumption for the separation of the catalyst and the products. The gas-phase heterogeneous oxidation may be an attractive process alternative. However, although the direct gas-phase oxidation of cyclohexane to cyclohexanol or cyclohexanone is thermodynamically possible [1], the selective cyclohexane conversion to oxygenated products under preservation of the C_6 molecular chain is not known until now. Alternatively, cyclohexane can be oxidized to cyclohexene, which can be further converted to valuable products. Many research efforts are focused in the last time to find new and selective catalysts [2–5]. We found that the supported nickel oxide is a very good catalyst for the selective oxidehydrogenation of cyclohexane to cyclohexene [5–7]. In order to develop new and better catalysts and to design catalytic reactors for oxidative dehydrogenation of cyclohexane, it is firstly necessary to develop kinetic models able to predict the effect of the temperature and reactants partial pressure on the cyclohexane conversion. Regarding the partial oxidation of cyclohexane in the gas phase on solid catalysts and its kinetic study, only a few reports are known so far [8–10]. In the present work the reaction network and the kinetics of cyclohexane oxidehydrogenation are investigated. The results offer a basis for understanding the reaction mechanism and for the process improvement by reaction engineering.

2. Experimental

2.1. Preparation and characterization of NiO/γ-Al_2O_3 catalyst

For the preparation of the NiO/γ-Al_2O_3 catalyst, a thermally pre-activated γ-Al_2O_3 consisting of nonporous particles (Degussa, C-type) was impregnated with an aqueous solution of nickel hexamminate at 318 K for 24 h under continuous stirring. The nickel loaded sample was washed with methanol for several times, filtered, dried at 393 K for 12 h and calcined

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at 873 K for 6 h. After a mechanical homogenization by grinding, the powder was pressed to pellets, crushed and sieved to the required particle size before being used in the reactor.

The catalyst was characterized by N_2 adsorption–desorption isotherm at 77 K after Brunauer–Emmet–Teller (BET) method, using a Sorptomatic 1900 FISONS instrument. The porosity and pore size distribution were obtained according to the Barrett–Joyner–Halenda (BJH) method. The nickel loading was analyzed by atomic absorption spectroscopy (AAS) using a Perkin-Elmer 4100 apparatus. The crystal phase composition was investigated using a HZG4 X-ray diffractometer. Temperature-programmed desorption (TPD) spectra were collected after exposing catalyst samples to cyclohexane at room temperature by using a quadrupole mass spectrometer (QTMS FISONS Instruments). The temperature was raised with 5 K/min from 290 to 723 K and kept here for 20 min. The mass quadrupole allowed data collection for up to six masses simultaneously in a single experiment.

2.2. *Catalytic tests*

The catalytic oxidation was performed by passing a gaseous mixture of cyclohexane in air over catalyst samples in a 200 mm long and 7 mm i.d. quartz tube reactor, which was electrically heated in a vertical furnace. For suppressing temperature gradients low cyclohexane concentrations in feed were used. Supplementary, the catalyst was diluted with inactive quartz split (1:4) having the same grain size as the catalyst. The temperature was measured with a 1 mm thick K-type thermocouple protected in a glass tube (internal diameter 1.5 mm; wall thickness 0.75 mm), placed axially in the center of the catalyst bed. The temperature at the reactor wall was measured with a similar thermocouple placed externally. The analysis of organic products was performed by on-line gas chromatography (HP5890 E II) employing a FFAP capillary column and a FID detector, in conjunction with an HPChemStation data collection package. CO and CO_2 were continuously analyzed with a BINOS IR photometer (Fisher–Rosemount). Blank runs performed with temperature raising from 483 to 853 K and GHSV (*gas-hourly-space-velocity*) from 5 to 60 l g^{-1} h^{-1} showed that under the experimental conditions used in this work the homogeneous reaction can be neglected.

Two experimental procedures were used in this study. Firstly, for the examination of the reaction pathways and the product distribution, integral measurements were performed. At a constant temperature of 663 K and a constant feed composition of 0.2 vol.% cyclohexane in air the GHSV was varied in the range of ca. 395–5 l g^{-1} h^{-1}. Secondly, for kinetic studies the reactor was operated in the differential regime. By keeping a constant flow rate of 48.4 l h^{-1}, the catalyst amount was varied to obtain conversions up to 10%. The inlet concentration of the cyclohexane was varied between 0.01 and 0.4 vol.%, and that of oxygen between 2 and 60 vol.%, in the temperature range of 513–723 K. Prior to kinetic investigations, the catalyst stability and the non-occurrence of internal and external diffusion limitations were checked.

3. Results and discussion

3.1. *Catalyst characterization*

The characteristics of the catalyst are summarized in Table 1. The catalyst support is a fumed γ-Al_2O_3, Degussa, C-type ($S_{BET} = 101$ m^2 g^{-1}) which is characterized as nonporous particles. The advantage of this support is that the nickel precursor is distributed mainly on the surface and not in the bulk of the support oxide. Thus, it was possible to obtain a catalyst with a nearby monolayer distribution of nickel oxide. The theoretical monolayer nickel oxide $n_{th} = 1.1$ was calculated by considering the nickel oxide loading (12.84%, w/w) and a shape projection space of 9.09 Å^2 corresponding to a NiO$\langle 1\ 0\ 0\rangle$ unit [11] reported to the catalyst surface. The catalyst porosity of 0.486 is interstitial porosity issued from the agglomeration and interconnection of the nonporous primary particle during catalyst preparation. The XRD patterns of both fresh and used catalyst showed mainly the crystal phase of γ-Al_2O_3 and weaker features of NiO. No crystalline metallic Ni could be identified by XRD investigations.

The TPD spectra of cyclohexane, cyclohexene, benzene and CO_2 following cyclohexane exposure of the catalyst sample are given in Fig. 1. Cyclohexane desorption starts at 298 K and develops after a first-order desorption kinetics with

Table 1
Chemical and morphological characteristics of the NiO/γ-Al_2O_3 catalyst

Support	γ-Al_2O_3 C, nonporous particle
Surface area support (BET) (m^2 g^{-1})	101
Surface area catalyst (BET) (m^2 g^{-1})	84
Nickel oxide loading (%, w/w)	12.84
Theoretical monolayer, n_{th}	1.11[a]
Porosity (BJH) (cm^2 g^{-1})	0.486

[a] Calculated with a shape projection space of 9.09 Å^2 corresponding to a NiO$\langle 1\ 0\ 0\rangle$ unit and reported to the catalyst surface.

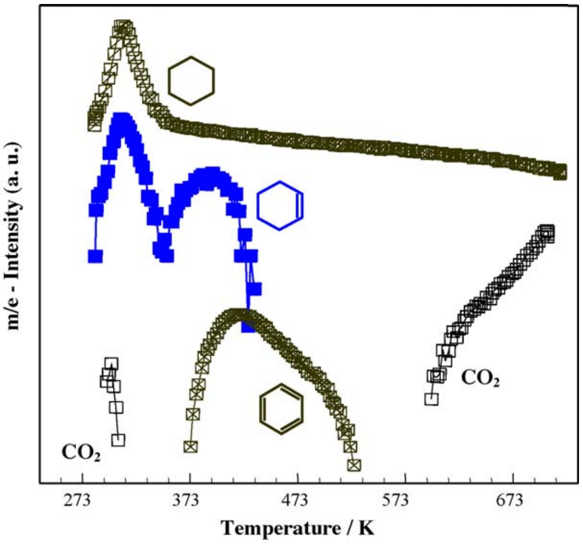

Fig. 1. Cyclohexane, cyclohexene, benzene and CO_2 TPD spectra after cyclohexane exposure of NiO/γ-Al_2O_3 catalyst at 298 K.

a maximum peak at 313 K. Above 373 K the cyclohexane desorption is negligible. The first products occurred are cyclohexene and CO_2. The TPD of cyclohexene shows two peaks centered around 313 and 393 K. This fact indicates that the generation of cyclohexene is stepwise [12] and takes place on two different kinds of active sites present in the alumina supported nickel oxide catalyst [1]. The benzene desorption starts at 378 K and shows a peak maximum at about 418 K, which corresponds to the end of the cyclohexene desorption. More interesting is the formation of CO_2. Its TPD spectrum shows a first relative small desorption peak in the temperature region from 308 to 323 K with a maximum at 313 K. The formation of CO_2 in this low temperature range occurs on the basis of the oxygen surplus present in the p-type semiconductor nickel oxide. After the complete consumption of this kind of oxygen species no CO_2 is formed. The generation of CO_2 starts again at about 590 K, when the temperature is high enough to yield the required energy for decomposing surface carbonate species. The occurrence of CO_2 in the gas phase is not likely to be limited by the reactivity of the nucleophilic (lattice) oxygen, since the second peak of cyclohexene yielded by the same oxygen species already occurs at 393 K. The formation of CO_2 can be continued up to complete reduction of nickel oxide, if the adsorbed hydrocarbon is sufficient. This behavior is an evidence for the oxidation of cyclohexane and its intermediate on two different ways: with electrophilic oxygen in the low temperature region and with nucleophilic oxygen in the high temperature region, respectively.

3.2. Catalytic tests

3.2.1. Preliminary investigations

The radial temperature gradient was no larger than 1 K and the axial temperature gradient in the catalyst bed was no more than 5 K. For the investigation of the catalyst stability, catalytic tests during several days at different feed compositions were performed. The results showed that by working with feed oxygen concentrations smaller than 12–15 vol.%, the relative catalyst activity decreased with 10–15% after 24 h. The cyclohexene selectivity became at the contrary higher. This means that from the practical point of view the operation of the catalyst in an optimal oxidation state could be a key for the process control. It is well known that with increasing the extent of catalyst reduction, the oxidehydrogenation selectivity increases while the activity of the catalyst decreases [13]. Nevertheless, for kinetic investigations the maintenance of a constant activity and good catalyst stability throughout all experiment is a crucial condition. On this reason we opted for the catalyst operation at higher oxygen concentrations. The dependence of the reaction rate on the oxygen concentration (not given) obtained by a differential operation of reactor and a constant cyclohexane feed concentration of 0.2 vol.% shown that the reaction rate is practically independent of the oxygen concentration above 15% for all reaction temperatures. The experiments at lower oxygen concentrations were strongly connected with a continuous change of catalyst state. An evaluation of the catalyst activity in these conditions was difficult and needs supplementary investigations.

The external diffusion effect was checked by monitoring conversion at 573, 663 and 723 K under various gas flow rates at a constant space velocity and a feed hydrocarbon concentration of 0.2 vol.% in air. The constant value of conversion obtained for all temperatures confirmed that the catalytic system was operated in the absence of diffusional limitations. The internal diffusion effect was checked by working with catalyst samples of different average particle diameter from 0.2 to 1.4 mm and monitoring the conversion. The results showed that below 0.7 mm the conversion was independent on the catalyst particle size. Therefore and to avoid high pressure drops we used in our experiments catalyst particles of 0.4–0.63 mm.

3.2.2. Integral reactor experiments

The oxidation of cyclohexane yielded cyclohexene, 1,3-cyclohexadiene and benzene as organic products as well as CO and CO_2 as inorganic carbon products. The selectivity-conversion patterns resulted from experiments in the integral reactor are shown in Fig. 2. The primary selectivities (the selectivities extrapolated to zero conversion) are 78% for cyclohexene, 4% for CO and 18% for CO_2 and are zero for 1,3-cyclohexadiene and benzene. According to the presented selectivity-conversion patterns, the gas-phase oxidative dehydrogenation on NiO/γ-Al_2O_3 catalyst starts as a three parallel reactions system leading from cyclohexane to cyclohexene, CO and CO_2 and develops as a parallel and consecutive reactions network, yielding also 1,3-cyclohexadiene and benzene which are further oxidized to inorganic products. Fig. 3 presents the reaction network associated to this oxidation process. Because of the low concentration level of 1,3-cyclohexadiene no formation of CO was taken into account for cyclohexadiene oxidation. The oxidation of benzene over nickel oxide catalysts leads to CO_2 only [14].

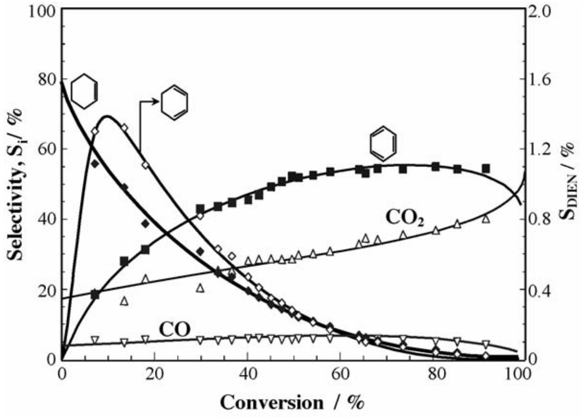

Fig. 2. Reactor selectivity as a function of cyclohexane conversion over NiO/γ-Al_2O_3 catalyst. Operations conditions: inlet gas 0.2 vol.% cyclohexane in air; GHSV = 4.7–395.2 l g^{-1} h^{-1}; T = 663 K.

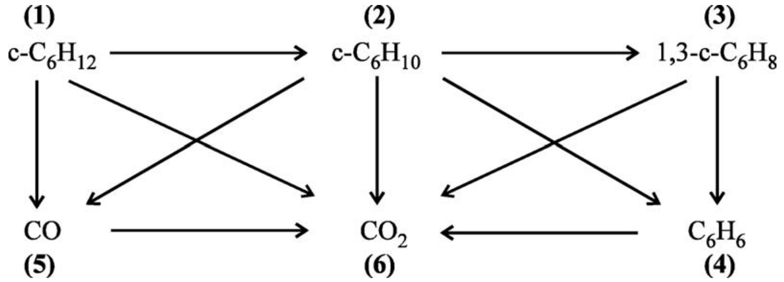

Fig. 3. Reaction network of the gas-phase cyclohexane oxidation over NiO/γ-Al_2O_3 catalyst.

3.2.3. *Differential reactor experiments*

The evolution of the cyclohexane reaction rate and the apparent formation rates of primary oxidation products as a function of the cyclohexane concentration are shown in Fig. 4A for 513 K and in Fig. 4B for 723 K, respectively. It is to remark that the evolution of the reaction rates is different for the given two temperatures. At low temperature both the cyclohexane reaction rate and the rate of cyclohexene formation obey the first-order kinetics in a large range of feed concentration of cyclohexane. In contrast of this, at high temperature both the cyclohexane and cyclohexene rates increase non-linearly with the cyclohexane concentration and suggest an inhibition at higher concentrations. The reaction order is smaller than 1. The CO_2 formation rate depends on cyclohexane only at very low cyclohexane concentrations and becomes weaker with the increase of the cyclohexane concentration. This behavior, together with the TPD spectrum of CO_2 at higher temperatures indicate that the formation rate of CO_2 is limited by the CO_2 desorption, at least at higher cyclohexane concentrations where the surface becomes covered with carbonate species. The rate levels are correspondingly different but the evolution of CO_2 is similar for both, low and high temperatures. CO formation is stronger dependent on the cyclohexane concentration than the CO_2 formation. Its lower level for both temperatures in comparison with other products (cyclohexene and CO_2) accounts for a small rate coefficient.

The kinetic experiments yielded cyclohexane reaction orders from 0.89 to 1.01 for the temperature range of 513–573 K and from 0.4 to 0.55 for 603–723 K, respectively. Similar values for cyclohexane reaction order of 1.0 on V–Mg–O catalyst at 713 K and 0.82 on $NdVO_4$, respectively were reported by Kung and Kung [10]. Moro-Oka reported a reaction order of 0.89 in propane by its oxidation on NiO at 623–689 K [15]. Our experimental found corroborated with the TPD results presented above are a strong evidence for the suggested mechanism change. For the further calculation of the specific reaction rate k_1 we adopt a cyclohexane reaction order $n_1 = 1.0$ for the temperature interval from 513 to 573 K and $n_1 = 0.5$ for 603–723 K, respectively. Fig. 5 shows the Arrhenius plots for the determined reaction constants versus reciprocal temperature. An alteration of the apparent activation energy from 36 kJ/mole in the temperature range from 513 to 573 K to 98 kJ/mole from 603 to 723 K takes place, which is a supplementary evidence for the suggested change of mechanism and for the nature of oxygen species involved (electrophilic and nucleophilic, respectively). For the oxidation of propane on NiO catalysts similar values of 109.7 kJ/mole in the temperature region 623–689 K [15] and 87.9 kJ/mole at temperatures higher than 503 K but only 29.3 kJ/mole at temperatures up to 503 K were reported [16]. The determined apparent frequency factors k_0 were 7.31 $l\,g^{-1}\,s^{-1}$ for the temperature region from 513 to 573 K and 8.79 $l^{0.5}\,g^{-0.5}\,s^{-0.5}$ from 603 to 723 K. Several authors reported a change of activation energy for CO oxidation [14,16–19] and for hydrocarbons oxidation [14,16]. Some of them [17,18] attributed this to the change in the magnetic properties of the NiO catalysts in the temperature region of the

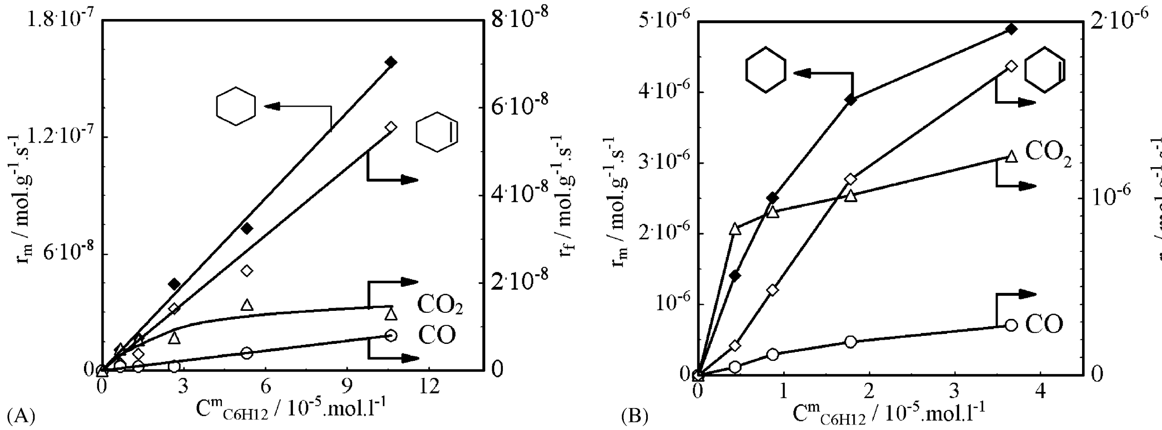

Fig. 4. Reaction and formation rates vs. cyclohexane concentration at 513 K (A) and 723 K (B). Conditions: $C_{O_2} = 20.38$ vol.%; $P_{reactor} = 1150$ hPa; total flow = 48.4 l h^{-1}.

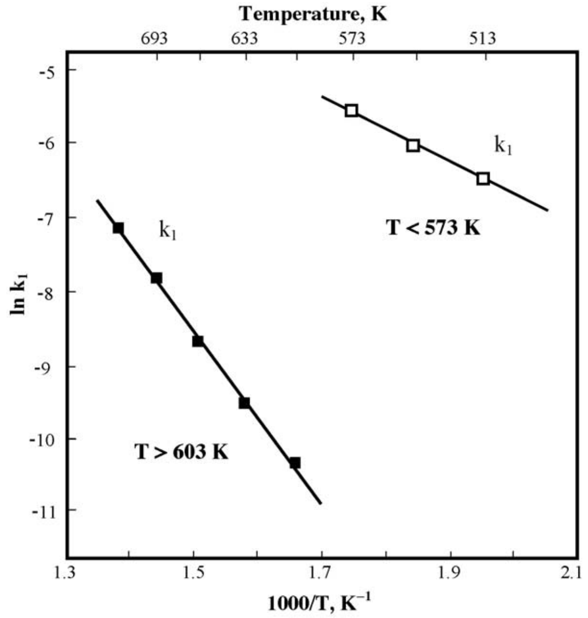

Fig. 5. Arrhenius plots of specific reaction rates k_1 calculated with a first reaction order in cyclohexane for the temperature region from 513 to 573 K and with a 0.5 reaction order for 603–723 K.

Néel point (543–573 K) [20]. By using different hydrocarbons, Yu Yao have determined changes of slops at different temperatures [16]. According to him, these changes are more probably a result from a shift in the rate determining step or reaction mechanism. Because of literature data gap regarding the mechanistic studies of gas-phase catalytic oxidation of cyclohexane we considered for our interpretation a large number of mechanisms proposed earlier for better studied alkanes [9,16,21–24].

For the interpretation of experimental results obtained in this work different reaction mechanisms derived from Langmuir–Hinshelwood, Eley–Rideal and Mars–van Krevelen kinetics are considered and analyzed. We propose two of them for the oxidation of cyclohexane on NiO/γ-Al_2O_3 catalyst. An Eley–Rideal mechanism in which the rate-limiting step is the surface reaction between dissociatively adsorbed oxygen on two active sites and cyclohexane from the gas phase is considered appropriate for the oxidation in the low temperature range. This will be detailed below. It is well-known that the nickel oxide is characterized as having an oxygen-rich stoichiometry [20,25,26]. The associative and dissociative adsorption of O_2 from the gas phase on the NiO catalyst with formation of electrophilic oxygen species is irreversible at low temperatures [27–29] and the equilibrium of surface defects is achieved very fast [30]. The oxidation state of the neighbored nickel cations changes from Ni^{2+} to Ni^{3+} and they are forced to a more stable octahedral coordination [20]. Two dissociatively adsorbed oxygen O^- on two neighbored Ni^{3+} cations and a surface defect can be considered as the active centre in the low temperature range. According to the mechanism proposed for similar alkanes [13,21,23,31], cyclohexane can be activated by the homolytic scission [32,33] of a C–H bond and abstraction of an H atom to form an adsorbed cyclohexyl radical and a surface OH group. The second electrophilic oxygen placed at a convenient distance abstracts the second H atom to generate adsorbed cyclohexene. The elimination of OH groups as H_2O, the cyclohexene desorption and oxygen adsorption is a condition for the restoration of the active center and the resumption of the catalytic act.

At temperatures above the Néel point of NiO the nucleophilic O^{2-} from the NiO lattice become reactive and can participate at the oxidation process. The abstraction of an H atom after a homolytic or heterolytic splitting of C–H bond is equivalent with the reduction of the nickel cation from the NiO catalyst. The oxygen leaves the catalyst lattice with the desorbed H_2O and/or oxygenated products. The reoxidation of the reduced nickel occurs by the gas-phase oxygen. The reduction–reoxidation cycle is repeated after a common Mars–van Krevelen mechanism [34] considered in earlier works [21,22]. The exact form of the reaction rate r corresponding to this mechanism type is given by Eq. (1):

$$r = \frac{k_{\mathrm{Red}} C_{\mathrm{C_6H_{12}}}}{1 + \frac{k_{\mathrm{Red}} C_{\mathrm{C_6H_{12}}}}{k_{\mathrm{Ox}} C_{\mathrm{O_2}}}} \qquad (1)$$

which yields the observed reaction order in cyclohexane. In Eq. (1), k_{Ox} and k_{Red} are the kinetic constants of the oxidation and reduction steps, and $C_{\mathrm{O_2}}$ and $C_{\mathrm{C_6H_{12}}}$ are the respective molar concentrations of oxygen and the cyclohexane.

4. Conclusions

The reaction pathway and the kinetics of the gas-phase oxidation of the cyclohexane on NiO/γ-Al_2O_3 catalyst were investigated. Cyclohexene is a primary product of the direct oxidehydrogenation of cyclohexane and undergoes consecutive transformations to cyclohexadiene, benzene and carbon oxides. Its selectivity decreases drastically with increasing conversion. The kinetics of the cyclohexane oxidation change, suggesting the occurrence of two different mechanisms involving electrophilic oxygen species at low temperature and nucleophilic oxygen species at higher temperature. The determined reaction orders of cyclohexane are 1.0 at 513–573 K and 0.5 at 603–723 K, respectively.

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