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VAPOR-PHASE OXIDATION OF CYCLOHEXANE

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ABSTRACT. In this review the reported literature data for the gas phase oxidation of cyclohexane are systematically presented and discussed. The production of oxygen-containing organic products by direct gas phase oxidation of cyclohexane is practically imposible, although it is allowed thermodynamically. Possibilities for the functionalization of cyclohexane towards valuable products such as cyclohexene or cyclohexadiene by gas phase oxidation over solid catalysts are emphasized.

CONTENS

1. INTRODUCTION

The basis of raw materials for the petrochemical industry changed decisively in the eighties. The use of previously disregarded paraffins and even of synthesis gas for the production of valuable chemical products is more and more envisaged as an alternative to the reactive but expensive and scarce olefins which were extensively used by now. In order to employ paraffins in the manufacture of chemicals, their activation or functionalization is necessary. With this respect the catalytic oxidation to oxygen-containing

products or the oxidehydrogenation of the paraffin leading to the homologous olefins are applicable, arising both the economic and the scientific interest [1-7]. Cyclohexane is an important basic material for many valuable intermediate products [8-10], whereby alone the production of cyclohexanol and cyclohexanone for the caprolactam production is for instance $1.6 \cdot 10^6$ to/year and that for adipic acid is $1.2 \cdot 10^6$ to/year [11].

Cyclohexanol and cyclohexanone were formerly manufactured from phenol but today the main raw material is cyclohexane. The oxidation is performed in the liquid phase with air by using homogeneous catalysts (H_3PO_4 or organic salts of Co^{2+} or Mn^{2+}). To avoid the further conversion of the desired products cyclohexanol/cyclohexanone to higher oxidized products, the reaction is driven at small conversion degrees (3-10 %). The necessity of recycling the unreacted cyclohexane, as well as the difficult separation of the products cause thereby high energy and capital outlays. The production of cyclohexanol/cyclohexanone from cyclohexene, although a very attractive process, has itself so far only little established [11, 12]. Reason for it is the difficult production of cyclohexene.

The production of cyclohexene from butadiene and ethylene is technically hardly realizable [13]. The cyclohexene selectivity achieved by partial hydrogenation of benzene is so far merely larger than 30 % [11]. The main product formed thereby is cyclohexane, which must be recycled to a new processing. By using another reaction route cyclohexene can be manufactured industrially by dehydration of the cyclohexanol both in liquid phase using sulfuric acid, and in the gas phase over alumina or alumosilicates after a cost-intensive technology [14]. Data regarding the direct functionalization of cyclohexane to cyclohexanol and cyclohexanone by a catalytic vapor-phase oxidation are not available within the present level of knowledge. On the basis of the literature data some new possibilities for the functionalization of cyclohexane can be envisaged, e.g. the oxidative dehydrogenation to cyclohexene and/or to 1,3-cyclohexadiene after the reaction (1):

(1)

The production of cyclohexene by the heterogeneously catalyzed oxidehydrogenation of cyclohexane could be thereby a new reaction way for the technical cyclohexanol/cyclohexanone production. At the same time new possibilities for the production of other technically interesting products arise, e.g. adipic acid, cyclohexene oxide, 1,2-cyclohexandiol, cyclohexyl aldehyde, cyclohexyl benzene etc. The oxidative dehydrogenation of cyclohexane to cyclohexene and cyclohexadiene is also scientifically very interesting. With this respect some promising research results were recently reported [15-17].

2. THERMODYNAMIC FEATURES OF CYCLOHEXANE OXIDATION AND OXIDEHYDROGENATION

In the gas phase system consisting of cyclohexane and air the following reactions become possible, which can be divided in cyclohexane oxidehydrogenation (2-4), oxidation (5-8) and dehydrogenation (9-11), as well as the reactions of the intermediate products (12-20).

Reactions of cyclohexane:

					$\Delta_r H^o_{298}$/kJ·mol^{-1} [18, 19]	
C_6H_{12}	+ 1/2 O_2	⟶	C_6H_{10}	+ H_2O	–124	(2)
C_6H_{12}	+ O_2	⟶	C_6H_8	+ 2 H_2O	–255	(3)
C_6H_{12}	+ 3/2 O_2	⟶	C_6H_6	+ 3 H_2O	–520	(4)
C_6H_{12}	+ 1/2 O_2	⟶	$C_6H_{11}OH$		–172	(5)
C_6H_{12}	+ O_2	⟶	$C_6H_{10}O$	+ H_2O	–349	(6)
C_6H_{12}	+ 6 O_2	⟶	6 CO	+ 6 H_2O	–1992	(7)
C_6H_{12}	+ 9 O_2	⟶	6 CO_2	+ 6 H_2O	–3690	(8)
C_6H_{12}		⟶	C_6H_{10}	+ H_2	+118	(9)
C_6H_{12}		⟶	C_6H_8	+ 2 H_2	+229	(10)
C_6H_{12}		⟶	C_6H_6	+ 3 H_2	+206	(11)

Reactions of the intermediary formed organic products:

C_6H_{10}	+ 1/2 O_2	⟶	C_6H_8	+ H_2O	–13	(12)
C_6H_{10}	+ O_2	⟶	C_6H_6	+ 2 H_2O	–396	(13)
C_6H_{10}	+ 11/2 O_2	⟶	6 CO	+ 5 H_2O	–1868	(14)
C_6H_{10}	+ 17/2 O_2	⟶	6 CO_2	+ 5 H_2O	–3565	(15)
C_6H_8	+ 1/2 O_2	⟶	C_6H_6	+ H_2O	–265	(16)
C_6H_8	+ 5 O_2	⟶	6 CO	+ 4 H_2O	–1737	(17)
C_6H_8	+ 8 O_2	⟶	6 CO_2	+ 4 H_2O	–3435	(18)
C_6H_6	+ 9/2 O_2	⟶	6 CO	+ 3 H_2O	–1472	(19)
C_6H_6	+ 15/2 O_2	⟶	6 CO_2	+ 3 H_2O	–3170	(20)

It would be desirable to bind oxygen atom in the cyclohexane molecule in such a way that the valuable products such as cyclohexanol or cyclohexanone develop according to the reactions (5) or (6). As shown by the reaction free-enthalpy as a function of temperature represented in Fig. 1 a, b after [16], the formation of cyclohexanol (5) and cyclohexanone (6) are thermodynamically possible by gas phase oxidation of cyclohexane in the

range of practice-usual temperatures. The formation of cyclohexanone (6) is even more favorable than the formation of cyclohexene (2) or cyclohexadiene (3) being exceeded only by the formation of benzene (4) (s. Fig. 1 a).

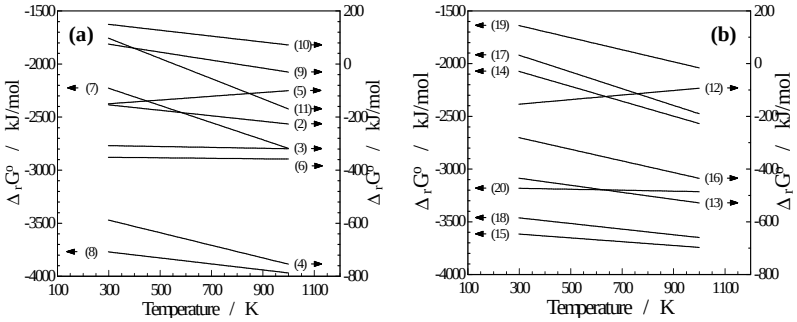


Fig. 1. Reaction free-enthalpy as a function of temperature for the reactions of oxidation, oxidehydrogenation and dehydrogenation in accordance with equations (2-20)

Despite the favorable thermodynamics, no results regarding the formation of cyclohexanol/cyclohexanone by gas-phase oxidation of cyclohexane are known so far. This fact could be explained by the much faster conversion of the formed intermediate products in the kinetically controlled cyclohexane activation, to the thermodynamically stable inorganic products. Here it must be noticed that the reaction free-enthalpy for the formation of the inorganic products is an order of magnitude higher than that for the formation of organic products.

In order to suppress the formation of benzene and the inorganic products, the kinetic control of the reaction is necessary. This is enabled by the use of suitable catalysts and of defined short retention times. The oxidative dehydrogenation of cyclohexane (2-3) is thermodynamically more favorable in comparison to the pure dehydrogenation of cyclohexane (s. Fig. 1 a). The formation of cyclohexadiene both by benzene hydrogenation and by cyclohexane dehydrogenation is thermodynamically unfavorable [18, 19]. However at higher temperatures the stability of the formed organic products is questionable. Within the oxidative dehydrogenation the thermodynamic driving force is increased and the conversion of cyclohexane to cyclohexene and/or cyclohexadiene is favored [18]. While the pure dehydrogenation is an endothermic process, in the presence of oxygen there is energy that is set free. Therefore, there are several processes known in the industrial practice where an endothermic reaction is coupled with an exothermic one, which supplies the necessary energy for the former. An example is the oxidehydrogenation of the methanol to formaldehyde over silver catalysts. Similar technologies were also developed for the dehydrogenation of

ethylbenzene to styrene. The oxidative dehydrogenation of cyclohexane is until now less known. For this reason systematic investigations regarding cyclohexane oxidation or oxidehydrogenation are interesting.

3. VAPOR-PHASE HOMOGENEOUS OXIDATION OF CYCLOHEXANE

3.1. Noncatalytic vapor-phase oxidation

On the search for improving the possibilities of manufacturing oxygen-containing organic compounds from oil products, cyclohexane already drew the attention of specialists. Estradare reported in 1933 [20] about the non-catalysed vapor-phase oxidation of a gas mixture consisting of cyclohexane and oxygen in a mole ratio of 1/4 in a glass tube filled with 3 mm glass rods. The lowest temperature of oxidation was 340 ℃. Per oxides were observed to form below that temperature but disappeared when the temperature was raised with 10-15 ℃ above it. Carbon monoxide and dioxide were both formed at 340 ℃, the maximum yield being at 400 ℃ of about 65 % CO and 18 % CO_2. By using a gas mixture of cyclohexane/air of 1/8 molar ratio in a quartz vessel of 24 mm diameter at 316 ℃ Ivan ov [21] has isolated a peroxide in the non-volatile liquid product. The waste gases contained 10.8 % O_2, 1.2 % CO, 5.6 % CO_2 and 0.7 % hydrocarbon. Hoot et al. [22] studied the kinetics of the gas phase oxidation of cyclohexane in a flow reactor, on a mixture of cyclohexane/air of 1/3 mol/mol with a contact time of 1.4 sec. The effluent gas was analyzed for CO, CO_2, O_2, water and aldehydes (determined as formaldehyde). Additionally cyclohexanone, pentanal, acrolein and acetaldehyde were detected in the condensed product mixture. The tests indicated the presence of acids, unsaturated hydrocarbons, peroxides, and cyclohexane oxide. The amount of oxygen containing organic products is very low and exceeds barely ca. 25 meq. per 100 g cyclohexane reacted. The presence of cyclohexene oxide was also suspected. By investigating the influence of reaction temperature on the product formation, the yield of CO, CO_2 and water achieved a maximum at approx. 380-400 ℃ . The effect of the residence time showed that an induction period was necessary for the reaction. This shows the accumulation of products, which causes the chain to branch (degenerate branching). The time for the induction decreases with increasing reaction temperature.

The formation of hydroperoxides during the gas-phase oxidation of cyclohexane [23] indicated the occurrence of the elementary reactions:

$$ROO\cdot + RH \longrightarrow ROOH + R\cdot \qquad (21a)$$

$$R\cdot + O_2 \longrightarrow ROO\cdot \qquad (21b)$$

. . .

An aldehyde or peroxide intermediate in this temperature region could play an autocatalytical role. It is known that the oxidation stability of aldehydes decreases with increasing temperature above 350 ℃. Increased temperatures would decrease the aldehyde concentration, which in turn decrease its autocatalytic effect. This can account for the decrease of total reaction rate in the temperature range 450 ℃ to 53 0 ℃. The test results have shown that during the gas phase oxidation of cyclohexane firstly aldehydes, among other formaldehyde, are formed, which are transformed in a subsequent reaction to CO and CO_2. At 410 ℃ benzene was also identified in a propor tion of 3 %, related to the reacted cyclohexane. Other oxygen-containing compounds occurred only when the reaction time was higher than 0.8 s. This shows the existence of an induction period. Furthermore a proportional dependence between the yield of oxidation products and the oxygen concentration in the gas mixture was determined. The increase of the ratio between the reactor surface and the reactor volume (A/V) of approx. 2 to 12 cm^2/cm^3 led to a clear inhibition of the cyclohexane oxidation. A further increase of the A/V ratio on approx. 28 cm^2/cm^3 did not influence the conversion rate. The investigations carried in order to clear up the reaction mechanism still permit, irrespective of its representation from today's view, the following conclusions:

- a number of single and consecutive reactions are possible in the vaporphase oxidation of cyclohexane;
- the reactions begin to accelerate after an induction period;
- the oxygen-containing organic products result from the autocatalytic oxidation on the basis of some peroxides formed in the incipient phase of the process;
- the yields of oxygen-containing products depend on the temperature, reaction time and feed composition.

3.2. Oxidation of cyclohexane by addition of gaseous additives

During the oxidation of n-alcanes having secondary C-atoms (propane, butane) in the presence of gaseous HBr as an activator, Bell et al. [24], Rust et al. [25] and Nawrocki et al. [26] achieved yields of carbonyl compounds up to 75 %. On the contrary in the case of cycloalcanes (cyclopentane, methylcyclopentane, cyclohexane) much smaller yields of carbonyl compounds were achieved, which is accounted for by the formation of condensation products under the effect of HBr. On the other hand the formed carbonyl compounds and other oxygen-containing intermediate products are less stable than the hydrocarbons. Nawrocki et al. [26] fed 15 ml/min HBr to a gas mixture of 30 ml/min gaseous cyclohexane, N_2 and O_2. These reactants were brought in a 450 cm^3 large glass bulb at 220 ℃. The following results were obtained:

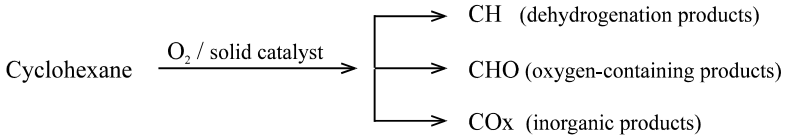
- the reaction consumed 40 % of the oxygen but only 8 % of this was accounted for as CO, CO_2 and H_2O;
- the oxidized mixture contained cyclohexanone and small amounts of diketones.

Hoot et al. [22] examined the effect of other activators in the gas-phase, like I_2 (0.3 wt. %), N_2O_4 (1.1 wt. %), $Pb(C_2H_5)_4$ (0.2 wt. %), aniline (1.0 vol. %), cyclohexylamine (1.0 vol. %), isoamyl nitrite (1.0 vol. %) and diethyl ether (1.0 vol. %) in the oxidation of cyclohexane. The composition of the product stream or the condensed products hardly differs from those without additives.

4. HETEROGENEOUS VAPOR-PHASE CATALYZED OXIDATION AND OXIDEHYDROGENATION OF CYCLOHEXANE

Few data were reported in the literature so far on the oxidation and oxidative dehydrogenation of cyclohexane over solid catalysts in the gas phase. The reason could be the failure of the attempts to insert oxygen atoms in the cyclohexane molecule and in particular the preservation of the 6-carbon ring against further oxidation. Although the formation of valuable products such as cyclohexanol, cyclohexanone and adipic acid by gas phase oxidation of cyclohexane is thermodynamically possible, no one has reported so far the formation of such products by the catalytic gas phase oxidation of cyclohexane. Berezin et al. [23] explained that the formation of valuable products by the gas phase oxidation of cyclohexane is improbable, in opposition with liquid phase oxidation, because of the completely different mechanisms. While the oxidation reaction in the liquid phase takes place at 120-140 ℃, a higher temperature of around 200 ℃ i s necessary in order to start the reaction in the gas phase. This causes a more intense C–C bond rupture so that the products of the gas phase oxidation contain less than 6 carbon atoms. The major products are therefore formaldehyde, CO, CO_2 and H_2O. However the authors do not deal with the important role of the catalyst.

The gas phase oxidation of cyclohexane can lead to organic products of oxidehydrogenation (CH), oxygen containing organic compounds (CHO) and inorganic products (CO_x) according to the reaction scheme (22).



(22)

In order to understand the possibilities and limits of the gas phase oxidation of cyclohexane and the factors controlling this process, the results reported in the literature will be discussed from the point of view of the oxidation products as presented in the above reaction scheme, but divided according to the main catalyst types.

4.1. Oxide supported metal catalysts

The oxidehydrogenation of cyclohexane over catalysts consisting on metals deposited on oxide carriers such as Pt/Al_2O_3 or Pd/Al_2O_3 is always accompanied by the deep oxidation to CO_2 [27, 28]. A small part of cyclohexane is dehydrogenated to cyclohexene and benzene. The selectivity to benzene decreases and the selectivity to CO_2 increase with increasing the partial pressure of O_2. In experimentally identical conditions the Pd/Al_2O_3 catalyst favors the total oxidation at variance to Pt/Al_2O_3, but the addition of CCl_4 to the reaction mixture leads to a decreasing activity and to an increasing selectivity to benzene [27]. The carbon balance and the appearance of the used catalysts showed the formation of coke as a result of cracking and molecular growth of the hydrocarbon species present [28]. No oxygenated organic compounds were identified.

4.2. Metal oxides

The oxidation of cyclohexane over unsupported metal oxides catalysts leads to the formation of inorganic products (CO, CO_2, H_2O) and dehydrogenation products (cyclohexene, benzene) in almost all works [22, 23, 30, 31]. Only a few authors reported the formation of small amounts of oxygen-containing organic compounds, usually maleic acid [23], and/or maleic acid anhydride [7, 23, 32]. Most of the results presented in the literature regarding cyclohexane oxidation on metal oxides [22, 23, 30-34] showed that the dehydrogenation reactions are always accompanied by the deep oxidation to inorganic compounds. For this reason these parallel reaction pathways will be discussed together, the control of the catalytic process towards one or another direction being considered as particular cases of a more general picture.

The unsupported metallic oxides catalysts, displayed in the Table 1, were examined by Hoot et al. [22] who found only CO_2 and H_2O as oxidation products of cyclohexane. As a measure for activity the lowest temperature of incipient reaction for the gas-phase oxidation of cyclohexane was indicated.

In another activity test, where the temperature to achieve a conversion grade of 80 % was determined during the cyclohexane total oxidation, Stein et al. [35] set up the following activity series for a set of metallic oxide catalysts:

$Co_3O_4 > Mn_2O_3 > Cr_2O_3 > NiO > TiO_2 > ThO_2 > \alpha\text{-}Fe_2O_3 > CeO_2 > CuO >$
$\gamma\text{-}Al_2O_3 > MgO > Pb_3O_4 > BeO > SiO_2 > WO_3 > V_2O_5 > ZnO > CaO > ZrO_2$

The different surface areas of the catalysts were however not considered.

Table 1

Catalysts and lowest temperature of incipient reaction for gas-phase oxidation of cyclohexane after Hoot et al. [22]

Catalyst	Lowest temperature of incipient reaction, ℃	Catalyst	Lowest temperature of incipient reaction, ℃
V_2O_5	240	V-Zeolite	336
Ag_2O	292[a)]	CoO	207
$CuCr_2O_4$	170 [b)]	MnO_2	342
$PbMoO_4$	297	ZrO_2	444
UVO_4	294	$Sn_3(VO_4)_2$	348
MoO_3	330	Shell 105 [c)]	340
Fe_2O_3	288		

Reaction conditions: Temperature T = 150-550 ℃, re tention time t = 0.2-12 s; $R_{cyclohexane/air}$ = 0.1-2 or 0.2-1.25 for Ag_2O and V_2O_5. [a)]Using water as a dilutant, lowest temperature of incipient reaction began at 503 ℃; use of 1 % cyclohexanone in cyclohexane feed lowered temperature to 198 ℃. [b)]1 % cyclohexanone was added to cyclohexane feed to act as reaction initiator. [c)]Dehydrogenation catalyst: $Fe_2O_3 \cong 70$ %, $Cr_2O_3 \cong 30$ %, $CuSO_4$ = 1 %, KNO_3 = 0.5 %;

By analysing the results obtained by Stein et al. [35, 36], Golodets [37] presented a correlation between the activity of oxide catalysts expressed as the temperature to achieve a conversion grade of 80 % (T_{80}) with the bonding energy of lattice oxygen of the oxide (q_s) (Fig. 2).

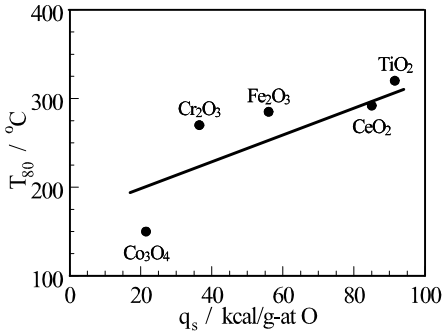


Fig. 2. A correlation of the catalytic activity for the oxidation of cyclohexane (T_{80} is the reaction temperature for 80 % conversion) with the bonding energy of lattice oxygen of the oxide, q_s [37]

After Margolis et al. [38] the catalyzed total oxidation of cyclohexane follows a second-order reaction rate. An activation energy of 158 kJ/mol was determined over a $MgCr_2O_4$ catalyst while over a $CuCr_2O_4$ catalyst it was 73.6 kJ/mol. The reaction order higher than 1 was not reproduced in the later experiments [30, 31].

Recent researches regarding the kinetics and mechanism of the total cyclohexane oxidation yielded a formal reaction order of cyclohexane of 0.8÷1.0 over $CuMn_2O_4$ and 0.65÷0.8 over $LaMnO_3$ in an oxidant reaction mixture (cyclohexane concentration between 0.01-0.40 vol. %) [31]. The apparent activation energy was of about 58 kJ/mol ($CuMnO_4$) and 56 kJ/mol ($LaMnO_3$). The partial pressure of oxygen has a slight influence only at lower temperatures (below 270 °C), at higher temperatures the reaction order of oxygen being close to zero. It was shown that the total oxidation was controlled at low temperatures by the surface reaction between electrophilic oxygen and adsorbed cyclohexane (a Langmuir-Hinshelwood mechanism) while at higher temperatures the rate controlling step was the reactive interaction of gas-phase cyclohexane with the surface oxygen species (Eley-Rideal mechanism).

At the same time, the experimental results suggest that the global oxidation process occurs by consecutive transformation reactions of cyclohexane (1) to cyclohexene (2) and benzene (3) and also by parallel oxidation reactions to CO (4) and CO_2 (5) after the network in Fig. 3.

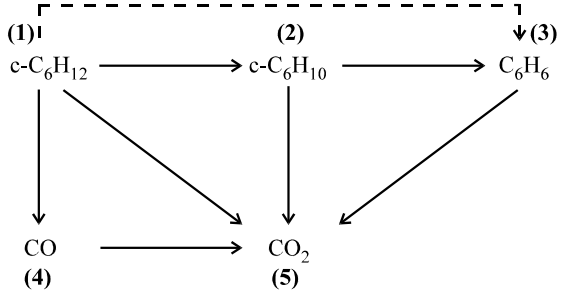


Fig. 3. The reaction network for the gas phase cyclohexane oxidation over $CuMn_2O_4$ after [31].

Under similar experimental conditions apparent activation energies of about 51 kJ/mole for Cr_2O_3 and 90 kJ/mole for ZnO were obtained [30]. The association of zinc and chromium cations inside the same oxide frame apparently led to no synergistic effect; thus, zinc chromite obeyed the rule of Boreskov [39]. The activation energy of about 83 kJ/mole indicated the predominance of the redox mechanism through lattice surface oxygen, although the electronic properties of $ZnCr_2O_4$ (p-type semiconductor, very

close to Cr_2O_3) should allow it to chemisorb easily oxygen. It is possible that the spinel lattice exposes less free chromium cations able to bound molecular oxygen than Cr_2O_3. A difference between $ZnCr_2O_4$ and Cr_2O_3 is the greater selectivity of the former towards organic products, especially benzene (Fig. 4, after [30]). Since as shown by electric measurements the electronic properties of the chromium-based catalysts are actually close it may be suggested that there are not the bulk properties, but the chemical nature of the oxide surface that decides the selectivity features of the catalyst.

As Kung et al. [5] have shown, the insertion of hard reducible cations in the lattice of an oxide catalyst (as for example, MgO in V_2O_5) led to an increase in selectivity towards dehydrogenation products. This fact is attributed to the oxygen atoms being bounded both to the reducible and to the hard-reducible cation, thus rendering them less disposable for an insertion in the organic molecule which is the first step towards total oxidation. This may be the source for the higher yield of dehydrogenation products in the case of zinc chromite. The low activation energy over chromium oxide indicated also an important share of the associative mechanism by electrophilic oxygen in the total oxidation rate [39]. The electronic properties of Cr_2O_3 as a p-type semiconductor allow the activation of a larger amount of electrophilic oxygen by adsorption of gas-phase molecular oxygen than over ZnO. The increase of the electrical conductivity value in air on going from the ZnO catalyst to the chromium based catalysts [30] may parallel their catalytic activity. The features of Cr_2O_3 and $ZnCr_2O_4$ are almost similar and very different from ZnO.

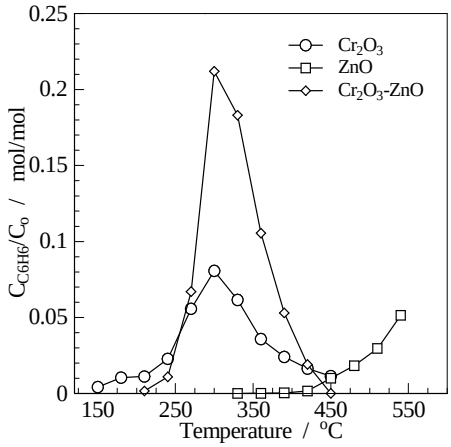


Fig. 4. The distribution of benzene (as organic product) as a function of reaction temperature (after [30]): m_{cat} = 0.5 g; d_p = 0.4-0.63 mm; $\dot{V}$ = 15.9 l · h^{-1}(NTP); C_o = 0.2 vol. % cyclohexane in air.

Michalakos et al. [40] and Kung et al. [41] found as appropriate catalysts for the oxidehydrogenation of cyclohexane to cyclohexene the magnesium vanadate, vanadium-magnesium mixed oxides and neodymium- and samarium vanadates. The reaction orders are very dependent on the nature of the catalyst. The order with respect to cyclohexane is first, and with respect to oxygen is zero on a Mg-V-O catalyst. The corresponding orders over $NdVO_4$ catalysts were 0.82 and 0.63. At low conversion degrees cyclohexene was the main product. The selectivity of cyclohexene was higher than 60 %, however only at conversion grades less than 5 % and sank immediately with increasing cyclohexane conversion. Benzene and carbon oxides were the other reaction products. Depending on the catalyst the selectivities amounted ca. 20-55 % for benzene and ca. 10-20 % for CO_x, whereby CO_2 was the main product of destructive oxidation. The examination of the oxidation behavior of cyclohexane and butane as compared with propane and isobutane [6, 34, 40-43] led to the following conclusions:

- the first product of the oxidehydrogenation process of a paraffin is the homologue olefin.
- the ability of the formed olefins towards further delivery of an allylic hydrogen atom determines the selectivity for the oxidehydrogenation product. The more difficult is the abstraction of allylic hydrogen or the formation of allyl species from the olefin over the catalyst surface (as in the case of propene and iso-butene), the larger is the desorption ability of the olefine, so that the intrinsic catalyst selectivity becomes larger. When the abstraction of allylic hydrogen is facile (butene, cyclohexene), the intermediary formed allyl complexes are easily transformed to further dehydrogenated products (dienes, benzene) and the selectivity towards olefines is lower.
- the selection of one or another reaction path (formation of dehydrogenated or oxygen-containing organic products or carbon oxides) depends on the topology of the catalyst surface or its active centers as well as on the type of the oxygen species (nucleophilic, electrophilic).

There are many catalysts known for their ability to insert oxygen or nitrogen into the molecules of lower chain paraffins C_3-C_5. Thus, acroleine [44-50], acrylonitrile [45, 48] and acrylic acid [51, 52] are produced from propane in two step processes. The maleic anhydride is obtained with high selectivities by oxidizing linear C_4 and C_5 paraffins over VPO [7, 32, 40, 53] and VMgO [40] catalysts. Unlike those, in the oxidation of C_6-C_7 alkanes significant amounts of cracking products are detected. The selectivity of maleic anhidride passes through a maximum. These observations suggest that the maleic anhidride formation observed in the oxidation of C_6 and C_7 alcanes does not derive from the primary oxidation of these hydrocarbons, but probably from the oxidation of the hydrocarbons (*i. e.* benzene) formed in the cracking of the C_6 and C_7 alcanes [7].

4.3. Supported metal oxides

Milas et al. [54] achieved for the first time in the 1930s an yield of maleic acid of approx. 20 % over a V_2O_5/pumice stone catalyst. The maleic acid was analyzed by titration and it can be assumed that the maleic anhydride formed in the reaction was hydrolyzed and determined as maleic acid. Formaldehyde, CO_2, H_2O as well as a small proportion benzene and benzochinone were also identified.

A systematic investigation of V_2O_5/TiO_2 supported catalysts by the oxidation of cyclohexane [32] showed that the modification of the carrier (anatase or rutile) as well as the number of the theoretical V_2O_5 layers on the carrier surface play an important role, both for the activity of the catalyst and for the product distribution [55]. The yield of maleic anhydride amounts up to approx. 50 % [32]. Phthalic anhydride, benzene and C_3-C_4 cracking products were also identified, but no oxygen-containing hydrocarbons with 6 carbon atoms.

In a recent publication Alyea et al. [15] reported on the oxidative dehydrogenation of cyclohexane using an oxygen/helium mixture over MoO_3 and MoO_3/γ-Al_2O_3 catalysts. The reaction products were cyclohexene, benzene, CO, CO_2 and H_2O. The ratio $C_6H_{12} : O_2 = 1 : 2.7$ was kept constant. By using cyclohexene as a reactant, benzene and the mentioned inorganic products were identified. Cyclohexadiene or oxygen-containing products were not found. Similarly to the oxidehydrogenation of other hydrocarbons over V_2O_5 [43, 56-58] the reaction occurs via a hydrogen atom abstraction from cyclohexane as the first step, which takes place on the Mo=O groups and leads selectively to cyclohexene [15].

It is generally accepted that nucleophilic oxygen species on the surface of oxide catalysts promote the partial oxidation reactions, whereas electrophilic oxygen adsorbed at the catalyst surface is responsible for the destructive oxidation, *i. e.* the formation of carbon oxides and water [59-64]. There are however situations where catalysts known for their capability to generate electrophilic oxygen are used for partial oxidation, in which case the limitation of the total oxidation is realized by kinetic control.

Chu et al. reported in a new publication [65] on the partial oxidation of methane to synthesis gas over NiO/γ-Al_2O_3 and NiO-La_2O_3/γ-Al_2O_3-catalysts. The increase of the NiO content from 10 %(wt.) to 17.5 %(wt.) caused a proportional increase in the yield of synthesis gas. A further increase of the NiO content to 20 %(wt.) led on the contrary to a reduction of the yield. The doping of the NiO with La_2O_3 (to 5 %(wt.)) did not bring clear modifications in the catalytic behavior. The formation of CO/H_2 is directly connected with the space velocity. At lower space velocity the oxidation of methane runs a successive reaction pathway, the CO/H_2 formed as an intermediate product being further oxidized to CO_2/H_2O. As

parallel reactions, the direct total oxidation of CH_4 and its conversion reaction (reformation) with water also take place. At higher space velocity the reformation reactions are suppressed and CO/H_2 and CO_2/H_2O are the products of the direct oxidation of methane in parallel reactions.

The results presented above and the interpretation from a new perspective of those reported by Mochida et al. [66, 67] led to the re-evaluation of the supported NiO catalysts, known earlier as total oxidation catalysts, as potential contacts for the selective oxidation of cyclohexane to cyclohexene [16, 17]. It has been shown that for the dissociation of the strong C–H bonding of the paraffinic cyclohexane molecule, the highly reactive electrophilic oxygen species on the surface of nickel oxide are of a great importance.

P-type semiconductors such as NiO are suitable for the generation of electrophilic oxygen species [62]. Their electron acceptor characteristics cause however the "emptying" of the adsorbed hydrocarbons of electrons. The consequence is a strong oxidation potential, which leads to the formation of total oxidation products, as it happens when nickel oxide is used as a catalyst for the destruction of volatile organic compounds. The presence of electrophilic oxygen species facilitates this oxidation. Therefore those catalysts have to be selected and manufactured that posses the ability to generate electrophilic oxygen species, but their electron acceptor characteristics or their bulk are nevertheless limited. A possibility to fulfill this demand consists of immobilizing a thin, if possible monomolecular layer of metallic oxide at the surface of an isolating carrier. Thus each NiO unit keeps its electron acceptor characteristic in detail, but these cannot however be extended over the lattice of the p-semiconductor oxide, which is missing, so that the electron acceptor ability is limited but the generation of electrophilic oxygen is still possible.

Within our preliminary investigations [16] on the oxidation of cyclohexane over a series of supported transition metal oxides, the NiO/γ-Al_2O_3 catalyst showed a unusual and so far unknown efficiency. Whereas over pure, carrier-free NiO (Merck) carbon monoxide and dioxide were the oxidation products as expected, an industrial nickel oxide/aluminum oxide catalyst (Harshaw, 0.2 % NiO/γ-Al_2O_3) yielded 3-17 % benzene. Additionally cyclohexene was also obtained with a selectivity of 5 %.

The analysis of the factors determining the catalytic properties of the supported nickel oxide and the possibility to control them, yielded the following conclusions:

- the catalytic characteristics of the NiO supported catalysts depend on the distribution and on the type of the NiO species formed on the carrier

- the formation and distribution of the NiO species of the active component as well as the strength of their interaction with the carrier are influenced by the following factors: the chemical nature and phase composition of the carrier, the pore morphology of the carrier, i.e. porosity and the internal geometrical structure of the pore system, the loading of the carrier with the active component; the thermal treatment of the green catalyst
- the working conditions during the oxidation process, the composition of the reactant mixture determines the oxidation state of the surface whereas the reaction temperature determines the type of reaction mechanism which the catalytic reaction follows.

We attempted to study the influence of the acidity of different carriers on the catalytic behavior of supported nickel oxide in cyclohexane oxidation [16, 68]. Two acid carrier, i.e. γ-Al_2O_3 and SiO_2, having different acid strength and MgO as strongly basic carrier were selected and examined systematically. Additionally SnO_2 as an oxygen acceptor was also tested as a carrier. The aim here was to check to what extent the catalytic oxidehydrogenation of cyclohexane can be controlled by oxygen mobility, by supposing NiO as an oxygen donor to SnO_2 as an oxygen acceptor.

A doubtless correlation between the activity of the examined catalysts and the specific surface or the Ni-content could not be determined. This fact is close to the assumption that the structure of the NiO species formed on the carrier surface as well as their interaction with the carrier play the crucial role for the conversion of the substrate and not the carrier surface. The formation and structural interaction of the NiO species with the carrier are related by all means to the carrier characteristics. The high activity of the NiO/SnO_2 catalysts having smaller surface area (Fig. 5 (a)) is surprising. This can be explained through to an oxygen-donor/oxygen acceptor synergy, which occurs at the boundary of the available NiO and SnO_2 phases. As a p-type semiconductor NiO possesses the ability to activate by adsorption gaseous oxygen [62, 69] thus behaving like an oxidation catalyst. The presence of an oxygen acceptor such as SnO_2 in the direct proximity of NiO enables the transfer of such very mobile oxygen species, which are responsible for the total oxidation of cyclohexane suppressing the desired partial oxidation. Thereby the presence of the oxygen acceptor improves the oxidehydrogenation reaction. A positive synergism of such mixed oxides having oxygen donor/acceptor interaction is exploited also in the selective oxidation of olefins [70] as well as in the oxidation of hydrogen or carbon monoxide [31].

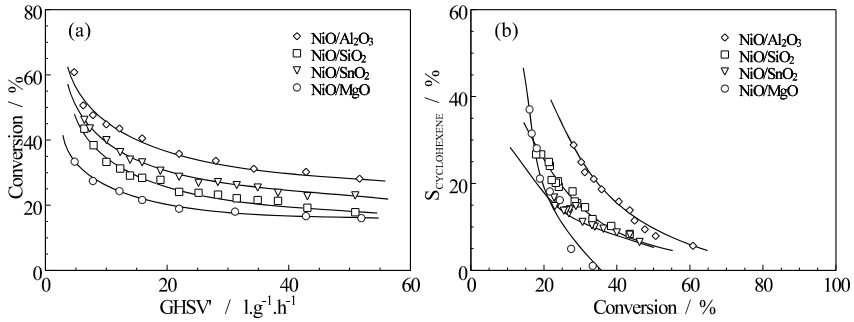


Fig. 5. Conversion (a) and cyclohexene selectivity (b) as a function of the space velocity in the oxidative dehydrogenation of cyclohexane over NiO supported catalysts, after [16]: NiO/γ-Al_2O_3 (91 m^2/g), NiO/SiO_2 (205 m^2/g), NiO/SnO_2 (5 m^2/g), NiO/MgO (29 m^2/g). Reaction conditions: feed concentration C_o = 0.2 vol. % cyclohexane in air; reactor temperature T = 390 ℃; catalyst grain size d_p = 0.4-0.63 mm.

Systematic investigations of the catalytic system NiO/γ-Al_2O_3 revealed a connection between the catalytic characteristics (activity, selectivity) and the structure of the NiO species formed on the catalyst surface. On the basis of the TPR, XRD, FTIR and Laser-Raman spectroscopy a new model was developed for the formation and structure of the NiO species over NiO/γ-Al_2O_3 catalysts, which allowed the understanding of their role in the cyclohexane oxidation. The following possible NiO species can be thereby regarded [16]:

- *bulk-NiO* crystallites
- *isolated NiO units* (oxidized single Ni atoms) on the surface of the carrier
- *bidimensionally NiO monolayer* developed on the top of the alumina carrier
- *surface nickel oxide species* incorporated in the surface of the carrier and having $NiAl_2O_4$ character
- *bulk-$NiAl_2O_4$* consisting of nickel cations which migrated deeply under the surface of the alumina carrier.

By comparing the catalytic results and the structural characterization of the catalysts it seems that the bi-dimensional NiO monolayer is responsible for both the activity (s. Fig. 6 (a)) and the conversion to cyclohexene (s. Fig. 6 (b)). The bulk $NiAl_2O_4$ caused a small activity or a small selectivity to dehydrogenation products. The presence of the bulk NiO species led to the complete oxidation.

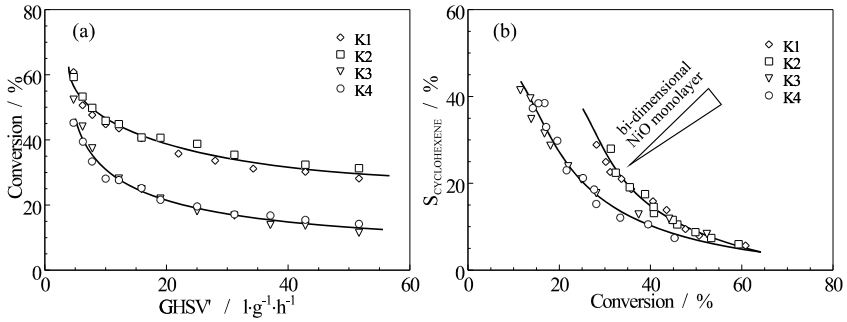


Fig. 6. Conversion as a function of the space velocity (a) and the selectivity in cyclohexene as a function of the conversion grade (b) during the oxide-hydrogenation of cyclohexane over the NiO/γ-Al_2O_3-catalysts after [16] (for description of K1-K4 catalysts s. text). Reaction conditions: inlet concentration C_o = 0.2 vol. % cyclohexane in air; reactor temperature T = 390 ℃; catalyst grain size d_p = 0.4-0.63 mm.

The distribution of the nickel species on the surface of the NiO/γ-Al_2O_3 carrying 2.54 wt.% NiO was changed during preparation by using different thermal treatments of the crude catalyst. As proved by TPR/TPO, XRD, FTIR- and Laser-Raman spectroscopy, the catalysts labeled as K1 and K2 on the one side, and K3 and K4 on the other displayed approximately the same surface structure. The increase of the calcination temperature from 600 ℃ (K1) to 750 ℃ (K2) caused firstly the dispe rsion of the NiO from the bulky phase on the carrier surface and its transformation into bi-dimensionally interlaced NiO species. This was also observed by Wachs *et al.* [71] in the case of other metallic oxide/carrier catalyst systems. A further increase of the calcination temperature to 900 ℃ (K3) or the p rolongation of the heating duration from 6h (K1, K2, K3) to 24h at 750 ℃ (K4) is accompanied by the formation of the crystalline $NiAl_2O_4$. At higher temperatures nickel from the upper layer of the carrier migrates inside the carrier.

The experimental results showed that the oxidation of cyclohexane over NiO/γ-Al_2O_3 catalysts is a structure-sensitive reaction. The positive effect of the bi-dimensionally interlaced NiO species is obvious. On the non-porous and highly crystalline γ-Al_2O_3 carrier (Degussa type C) the bi-dimensional NiO monolayer species were preferably formed and the catalyst showed the highest activity and selectivity to cyclohexene. Oppositely, the migration of the Ni-cations in the structure of the carrier and the formation of $NiAl_2O_4$ were facilitated by a porous and weakly crystallized structure of the γ-Al_2O_3 carrier, with a higher number of structural defects.

The analysis of the selectivity-conversion patterns after the method developed by Riekert [72] and Kotter et al. [73] allowed the determination of the reaction pathways for the conversion of the chemical species present

during the oxidation of cyclohexane. A strong decrease of the cyclohexene selectivity with increasing conversion was determined, which points out to a stability parameter [72] of cyclohexene smaller than one. This is explained by large conversion rates to 1,3-cyclohexadiene, benzene or carbon oxides. The clear tendency of the initial benzene selectivity towards zero, as well as the shape of the selectivity curve of 1,3-cyclohexadiene with a maximum, is a strong hint of the indirect formation of benzene over cyclohexene or 1,3-cyclohexadiene. The relatively low level of the cyclohexadiene concentration in the gas phase could arise from its small desorption rate that leads to its further oxidehydrogenation. With the increase of the cyclohexane conversion over 75 % (low space velocity) the condition are created for the oxidation of benzene to CO_2, so that the benzene selectivity decreases. The formation of CO from the 1,3-cyclohexadiene can be neglected on the basis of the low concentration of this intermediate in the gas phase. The carbon monoxide already existed in the reaction system (probably by the conversion of cyclohexane and cyclohexene) before the formation of 1,3-cyclohexadiene occurred. On the basis of experimental results the reaction network represented in Fig. 7 could be settled [16] for the oxidation of cyclohexane over a $NiO/\gamma\text{-}Al_2O_3$ catalyst. The conversion of cyclohexane (1) begins as a process with three parallel reactions to the products cyclohexene (2), CO (5) and CO_2 (6) and develops to one with parallel and successive reactions towards carbon oxides with 1,3-cyclohexadiene (3) and benzene (4) as intermediary products.

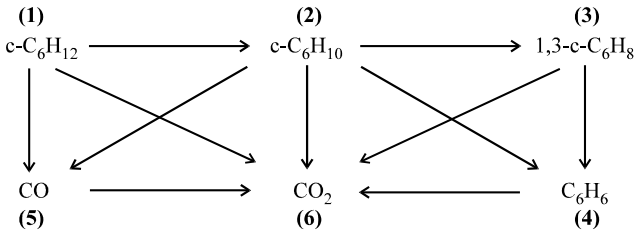


Fig. 7. The reaction network by cyclohexane oxidation over $NiO/\gamma\text{-}Al_2O_3$

4.4. Egg-shell oxide catalysts

The selectivity towards partial oxidized [74-76] or hydrogenated [77] products can be improved when using egg-shell-type catalysts with regular pore system, that is having pores with defined dimensions [78, 79]. In order to increase the selectivity to the desired target product cyclohexene, the possibilities for the production of egg-shell-type catalysts with as high surface area as possible and at the same time short and wide far pores were explored, in order to suppress the influence of the pore diffusion of the components and thus its influence on the product selectivity. In the classical manufacturing processes of egg-shell-type catalysts by the anodic oxidation from wire

sticks or metal plate pieces in the Faraday range, followed by impregnation [75-77, 81] the formation of the active component in the oxide egg-shell is a crucial process for the catalytic effectiveness of the catalyst. Because of the small stability of the oxide matrix formed by anodic oxidation towards acid or basic solutions [80, 81], the selection of the precursor of the active component is a difficult point. Here it must also be taken into account the fact that the catalyst manufacture processes involving many steps are critical from the point of view of the reproducibility.

A new procedure, the anodic oxidation under spark discharge (ANOF) [82], proved itself suitable to avoid these disadvantages. It was developed for the production of oxide coatings on barrier layer-forming metals, like aluminum, titanium, tantalum, niobium, zircon, magnesium etc. and it was successfully applied [17, 82-84]. Due to the particular art of shell formation, the pore sizes, the layer growth and the active component doping, reproducible layer systems can be produced in one single process step. By appropriate selection of the aqueous electrolytes and the coating parameters the egg-shell-type catalysts can thus be manufactured having desired layer composition, and continuous pore system. In Fig. 8 a SEM picture of the surface texture of the catalyst is $NiO/Al_2O_3/Al$ is shown as an example.

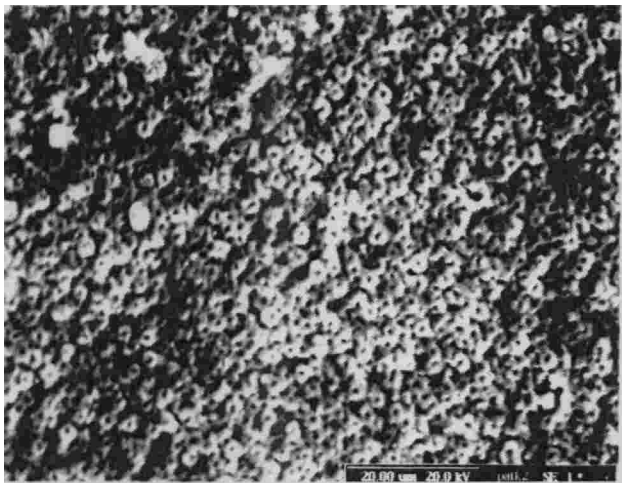


Fig. 8/ SEM photography of the surface structure of the catalyst $NiO/Al_2O_3/Al$ [85].

Such egg-shell-type catalysts on metallic wire sticks such as $NiO/Al_2O_3/Al$, $NiO/TiO_2/Ti$ or lithium doped $NiO\text{-}Li_2O/Al_2O_3/Al$, manufactured by ANOF, have proven themselves as suitable in the oxidative dehydrogenation of cyclohexane to cyclohexene [85]. In Fig. 9 the conversion grade of cyclohexane and the product selectivities as a function of temperature on a $NiO/Al_2O_3/Al$ are represented.

The special feature of the ANOF manufactured $NiO/Al_2O_3/Al$ catalysts consists of the fact that the NiO active component on the catalyst surface is distributed as a bi-dimensional layer, without the formation of "bulk NiO". Thus the prerequisites for the selective attack of the electrophilic oxygen species formed on the oxide catalyst surface are realized and the cyclohexene formation is favored. The doping of the $NiO/Al_2O_3/Al$ catalyst with low valence Li supports the formation of electrophilic oxygen species, so that the activation of cyclohexane is facilitated [85].

The decrease of the cyclohexene selectivity with increasing temperature (Fig. 9) is probably due to its oxidation with formation of 1,3-cyclohexadiene or benzene as products of the successive oxidehydrogenation. The formation of 1,3-cyclohexadiene with a selectivity of up to 3-5 % is remarcable. The CO selectivity is situated within the range of 0-4 % and does not change substantially with the temperature. The shape of the CO_2 selectivity curve as a function of the temperature is unusual. On the $NiO/Al_2O_3/Al$ catalyst the conversion amounts approx. 30 % at 330 ℃, than sinks to approx. 24-25 % in the temperature range of 390-450 ℃ and then rises continuously with the temperature up to approx. 32 % at 530 ℃.

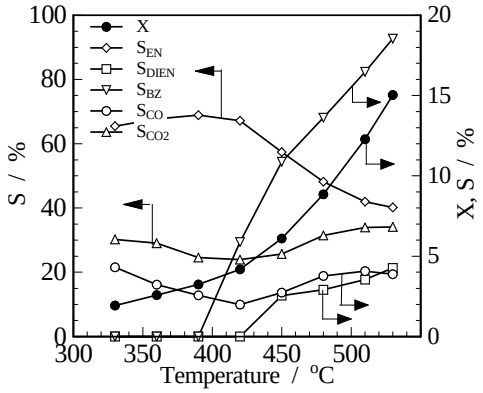


Fig. 9. Cyclohexane conversion and distribution of reaction products as a function of temperature on the $NiO/Al_2O_3/Al$ catalyst; m_{cat} = 0.5 g; $l_{cat}x\phi_{cat}$ = 4.0x1.0 mm; $\dot{V}$ = 15.9 $l \cdot h^{-1}$(NTP); C_o = 0.2 % (vol.) cyclohexane.

The experimental findings for the CO_2 selectivity on the catalysts $NiO/Al_2O_3/Al$ and $NiO\text{-}Li_2O/Al_2O_3/Al$ suggest a change of the oxidation mechanism at temperatures between 330-400 ℃. In the low temperature range a mechanism involving electrophilic oxygen species is probably occurring, while in the higher temperature range a redox mechanism of the Mars-van Krevelen type takes place, assisted by the nucleophilic oxygen species, similar to the model proposed by Bielanski and Haber [62]. The

temperature range for the change of the oxidation mechanism is connected to the magnetic properties of NiO as revealed by the work of Cimino et al. [89] and Bielanski et al. [90]. Thus, in the Néel temperature domain the magnetic transition of the nickel oxide containing catalysts and the disappearance of the rhombohedral deformation of the cubic lattice of NiO takes place [86-88].

4.5. Ion-exchanged zeolites

There are some few work dealing with the oxidation of cyclohexane over ion-exchanged zeolites [66, 67, 91-93]. Mochida et al. [66] examined the oxidation of cyclohexane over transition metal oxides ion-exchanged NaY zeolites. Up to 350 ℃, benzene and carbon mono xide were the main products, and also a small amount of cyclohexene. Above 350 ℃ other products were also observed, as acetic acid and propionic acid. The Cu(II)-Y was found to be the most selective catalyst for benzene formation among Cr(III), Ni(II) and Ag(I) exchanged Y zeolites. Pd(II)-Y had the largest activity for the formation of carbon dioxide.

The kinetic study of cyclohexane oxidation over Cu(II)-NaY-catalyst [67] showed a low dependence of the formation rate of benzene and CO_2 on cyclohexan partial pressure, in a reactant mixture containing 0.05 to 0.95 atm oxygen and 0.01 to 0.18 atm cyclohexane. The reaction order of oxygen was 1 for the formation of benzene and 0.5 for the formation of carbon dioxide. The determined apparent activation energies over the Cu(II)-NaY catalyst amounted to approx. 113 kJ/mol for the formation of benzene and approx. 122 kJ/mol for the formation of CO_2. For the other exchanged zeolites the corresponding values ranged 40-113 kJ/mol and 52-149 kJ/mol, respectively. The reaction occurred at small conversion grade in the form of a parallel reaction (formation of CO_2 and benzene), but with increasing conversion other parallel and successive reactions took place.

To clear-up the influence of the metal loading of the zeolites on the possible reaction pathways, the oxidation of cyclohexane over Cu(II)-NaY was firstly examined [67]. Upon the increase of the loading with Cu^{2+} cations, a higher conversion rate of cyclohexane was found. The selectivity to cyclohexene decreased however very strongly and became almost zero by over 20% (wt.) copper loading. That means that while Cu^{2+} cations represent the active sites for oxidation, the presence of not-exchanged Na^{+} cations may be beneficial for the selective formation of cyclohexene. The formation of benzene occurs both through cyclohexene (at small conversion grades) and directly from cyclohexane, in each case in competition with the formation of CO_2. The rate of CO_2 formation is independent of the exchange degree of the zeolite. That means that the responsible oxygen species are connected with the zeolite itself and not with the exchanged cations. This

findings are conform with the results of Minachev et al. [92, 93], who have shown that the oxidative dehydrogenation of cyclohexane can occur in the presence of alkaline cation-exchanged zeolites of type A, L, chabazite, erionite and mordenite containing no transition metals with cyclohexene as the major product.

In order to investigate the role of the reactants in the oxidation process [67], the Cu(II)-NaY catalyst was firstly saturated at 320 ℃ either with cyclohexane, or with oxygen, or with both. Then the corresponding second reactant, oxygen or cyclohexane or helium as a flushing gas was admitted in form of pulses. Based on the observed results it was concluded that the chemisorption of the less reactive cyclohexane blocked the copper active centers and the O_2 adsorption became thus the rate-determining step. On the catalyst surface cyclohexane formed weakly and strongly adsorbed species. While the reaction of weakly adsorbed cyclohexane with associatively adsorbed oxygen species led to benzene, the strongly adsorbed cyclohexane yielded together with dissociatively adsorbed oxygen mainly CO_2. Associative as well as dissociative oxygen may be present on Cu(II)-Y, however, it is plausible to assume associative oxygen as the reactive species for benzene formation in this oxidative dehydrogenation.

These conclusions are partially in contradiction to the theory of Haber [59-61] over the role of the electrophilic or nucleophilic oxygen species in determining the reaction pathway in oxidation reactions. His works pointed to the electrophilic O_2^- and O^- as responsible for splitting the C–C bond and causing a further oxidation. The nucleophilic O^{2-} bound at the transition metal cations was taken as responsible for the partial oxidation with or without oxygen insertion.

On the basis of the present level of knowledge, the experimental results published by Mochida et al. [67] can also be differently interpreted: The independence of the CO_2 rate of formation on the Cu loading can be due to the presence of the O_2^- and O^- species at the surface of the Cu(II)–NaY catalyst. The existence of such oxygen species on a copper free zeolite surface was already proven by Wang and Lunsford [94] by the ESR technique. This explains the independence of the CO_2 rate of formation on the degree of loading of NaY zeolites with Cu^{2+}. The existence of the Cu^{2+} ions in the zeolite lattice enables the dissociative chemisorption of oxygen and the formation of O^{2-}, which is responsible for the oxidehydrogenation of cyclohexane to benzene. The formation of cyclohexene is favored by the strongly basic centers, which are likely to take a proton off from cyclohexane. The second hydrogen atom from the carbocation could be delivered under the influence of, for example, an electrophilic oxygen species (O_2^-, O^-) in a second step as H^-. That could explain the formation of cyclohexene already over zeolites having only a small exchange degree of sodium with copper

cations. The participation of electrophilic oxygen species to the selective oxidehydrogenation was stated also by Tagawa et al. [95, 96] during the oxidative dehydrogenation of ethylbenzene to styrene.

The experimental findings of Minachev et al. [92] during the investigations of cyclohexane oxidehydrogenation over alkaline cation-exchanged zeolites suggested that a surface reaction between adsorbed cyclohexane and only slightly adsorbed molecular oxygen was the limiting process step. The reaction rate was directly proportional to oxygen partial pressure while the order of cyclohexane reaction was below unity and was described by the equation:

$$r = \frac{k \cdot P_{O_2} \cdot P_{C_6H_{12}}}{1 + a_{C_6H_{12}} \cdot P_{C_6H_{12}}} \qquad (23)$$

The determined apparent activation energy was 23 kJ/mole and the heat of adsorption of cyclohexane 12.5 kJ/mole. The catalytic runs were performed at 300-500 ℃ and at cyclohexane partial pressure of 0.05 to 0.3 atm and oxygen partial pressure of 0.05 to 0.18 atm.

Alimardanov [91, 97] reported results on cyclohexane oxidation over H–Mordenite (degree of decationization ca 75 %) modified with Fe_2O_3 und Gd_2O_3 in a quantity of 50% (wt.). The condensed liquid product contained cyclohexane, cyclohexene, benzene and methylcyclopentene isomers. Carbon dioxide and C2-C3 hydrocarbons were found in the gaseous product. Hydrogen and carbon monoxide were detected too, but their concentration were insufficient for their accurate determination. After distilling at 90 ℃ the liquid reaction product, in the condensed water layer the following oxygen-containing compounds were found: epoxycyclohexane, epoxymethylcyclopentane, cyclohexanol, methylcyclopentanols, cyclohexenol, cyclohexanone, cyclohexenone. Their amount did not exceed 0.5-0.7 % of the total weight. No other publication reported by now the formation of oxygen containing C_6 products upon gas phase oxidation of cyclohexane. The interpretation of the results yielded a reaction scheme composed of parallel and successive reactions. The formation of cyclohexene is described by a first order kinetics reported to cyclohexane and 0.5 with respect to oxygen, while for the formation of benzene the orders were both 1. A reaction mechanism for the oxidehydrogenation of cyclohexane by means of nucleophilic oxygen species O^{2-} was suggested. For the formation of oxygen-containing organic compounds a reaction mechanism was postulated, which contained both catalytic and homogeneous reaction steps.

5. GENERAL REMARKS

The technical purpose of gas phase cyclohexane oxidation may be either the partial oxidation for the manufacture of functional derivatives of cyclohexane by preserving the six atom ring, or the total oxidation yielding selectively CO_2 and H_2O as products when the removal of cyclohexane vapor from residual gases is desired. Although thermodinamically possible, gas phase oxidation of cyclohexane yields no oxygen containing organic compounds, both in the presence and in the absence of catalysts and/or additives. This fact can be attributed to the much higher rate of destruction of the oxygen containing compounds than the rate of their generation. At the present state of the art in the field, the formation of cyclohexene and casually of cyclohexadiene remains the only possibility of oxidative gas phase functionalization of cyclohexane. This transformation occurs by means of electrophilic or nucleophilic oxygen species generated by oxide, supported oxide or modified zeolite type catalysts.

If one admits that the process of catalytic oxidation involves the continuous switch of the oxidation state of the active center, we may consider that whatever the type of oxygen species that are involved in the oxidation (electrophilic or nucleophilic) is, the catalytic reaction is mirrored by the redox cycles of the active site. The rate of the catalytic reaction may thus be expressed as the turnover frequency of the reduction/reoxidation of the catalyst.

While the re-oxidation of the reduced active centers of the catalyst takes place only by the gas phase oxygen, the reduction of the active centers takes place both via cyclohexane and via all formed intermediate products. If the chemisorption of cyclohexane is the rate-determining step and the concentration of other components is very small [6, 16, 40-42, 57, 64, 100-102], the reduction rate of the catalyst under participation of other components may be neglected in comparison to that of cyclohexane. The reduction rate r_{Red} and re-oxidation rate r_{Ox} are then described by the equations (24) and (25), respectively:

$$r_{Red} = k_{Red} \cdot P_{C_6H_{12}} \cdot \Theta_{Ox} \tag{24}$$

$$r_{Ox} = k_{Ox} \cdot P_{O_2} \cdot \Theta_{Red} \tag{25}$$

where: k_{Red}, k_{Ox} are the rate constants of the reduction or the re-oxidation; $P_{C_6H_{12}}$, P_{O_2} are the partial pressures of cyclohexane and oxygen; Θ_{Ox}, Θ_{Red} are the proportions of oxidized or reduced active centers.

In the stationary state:

$$r_{Red} = r_{Ox} \tag{26}$$

and the total reaction rate *r* becomes:

$$r = \frac{1}{\frac{1}{k_{Red} \cdot P_{C_6H_{12}}} + \frac{1}{k_{Ox} \cdot P_{O_2}}} \tag{27}$$

For the eq. (27) two limit situation may occur:

Case I

$$k_{Red} \cdot P_{C_6H_{12}} >> k_{Ox} \cdot P_{O_2} \tag{28}$$

The eq. (27) can then be simplified as eq. (27a). The oxidation rate of the reduced catalyst becomes the rate-determining step with kinetics of first order concerning oxygen and zero-order concerning cyclohexane.

$$r = k_{Ox} \cdot P_{O_2} \tag{27a}$$

The situation corresponds to the oxidation over a difficult oxidizable catalyst or an oxygen-poor gas mixture. The catalyst operates in the predominantly reduced status.

Case II

$$k_{Ox} \cdot P_{O_2} >> k_{Red} \cdot P_{C_6H_{12}} \tag{29}$$

The reduction rate is determining for the kinetics of the whole process and eq. (27) becomes (27b).

$$r = k_{Red} \cdot P_{C_6H_{12}} \tag{27b}$$

The reaction is first-order regarding cyclohexane and zero-order order regarding oxygen. The catalyst works in a highly oxidized state.

As a matter of fact, during the catalytic process the catalyst changes its oxidation state within some limits [34, 55, 103-106] and the experimental determined values are in much cases temporary ones which lay between those limits.

To understand the role of the catalyst as a key factor of the oxidation process we shall describe on the basis of the simplified scheme in Fig. 10 its transformation to cyclohexene in a first stage. The further transformation of cyclohexene occurs then similarly.

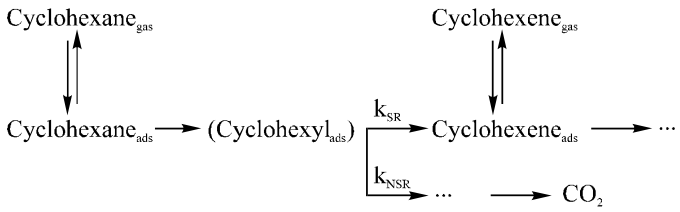


Fig. 10 Reaction scheme of cyclohexane oxidation

The cyclohexane oxidehydrogenation begins by the adsorption of cyclohexane molecule at an active center. According to the mechanism for the oxidehydrogenation of paraffins and cycloparaffins suggested in [40, 41, 98, 99], the attack of the oxygen at a C–H bond and the abstraction of an hydrogen atom is the first step of the surface reaction. Investigations for the oxidehydrogenation of paraffins showed that the dissociative chemisorption with splitting the C–H bond is the rate-determining step [6, 16, 40-42, 57, 64, 100-102]. In the case of cyclohexane oxidation under co-operation of nucleophilic lattice oxygen after a redox mechanism of the type Mars and van Krevelen [108], in conformity with literature data [6, 41, 91, 107], where the formation of carbo-ions as surface intermediate products occurs, the catalyst undergo a redox process, which is not discussed here. For the oxidehydrogenation of cyclohexane over a series of metal vanadates, Chaar et al. [42] and Patel et al. [34, 100] suggested a homolytic C–H splitting, which shall be considered here. This process yields a cyclohexyl radical, which is stabilized by the capture of the available electron to the incompletely filled d–d orbital of the metal (coordinative bonding) or by fixation in a neighbouring oxygen vacancy. The cyclohexyl radical has two possibilities to interact with oxygen species:

1) the attack of the oxygen at the C_β–H bonding and formation of cyclohexene, which remains adsorbed by its p-electrons at the oxygen vacancy;
2) attack of the oxygen at the carbon skeleton (C–C bond) and formation of carbon oxides.

The catalyst is in both ways reduced. The formation of dehydrogenation products is called selective reduction of the catalyst and has the rate constant k_{SR}. Similarly the formation of inorganic products (CO_x, H_2O) by the non-selective reduction of the catalyst has the rate constant k_{NSR}. The cyclohexene formed has to be desorbed as fast as possible, in order to avoid the further conversion, according to a rake model [60]. The rate of the further oxidehydrogenation of adsorbed olefins depends on their ability to build allylic alkyl species and is thereby greater for cyclohexene then for linear

C3-C6 olefins [40, 41]. With the increase of the dehydrogenation degree, the adsorption tendency of the intermediates formed also rises. In this way the oxidehydrogenation of cyclohexane (under co-operation of two oxygen atoms) will probably lead merely to benzene (with ist stable aromatic structure) than to cyclohexene [98].

By taking into account the reaction network in Fig. 10, the maximal cyclohexene selectivity of the catalyst (intrinsic selectivity) S_{EN} can be expressed as the ratio between the rate of selective reduction of the catalyst and that of the non-selective reduction:

$$S_{EN} = \frac{r_{SR}}{r_{SR} + r_{NSR}} \tag{30}$$

The catalyst selectivity for cyclohexene formation is always superior to the selectivity of the reactor as yielded by experiments [72]. The cyclohexene selectivity expressed by eq. (30) is the maximum value that the catalyst could achieve in the absence of successive transformation of cyclohexene or of mass or heat transfer limitations.

In order to obtain high selectivity of cyclohexene, the non-selective reduction of the catalyst should be avoided. This requires to maintain the catalyst at a low oxidation degree as shown by Andersen et al. [103]. This poses problems regarding the on-stream stability of the catalyst [99]. Practically, the only remaining possibilities remain either the appropriate combination of active components, which encompasses eventually most of the present researches, or the control of the oxidation state of the catalyst by optimizing the ratio between cyclohexane and oxygen in the gas phase.

6. CONCLUSION

The data discussed in this review show that the functionalization of cyclohexane by gas phase oxidation can be achieved with satisfactory results only in the presence of catalysts. The most interesting products are cyclohexene and 1,3-cyclohexadiene. The other possible oxidation products are benzene and carbon oxides. No oxygen containing products were reported except for ref. [91], but there were also to low amounts obtained to be quantified.

A wide range of catalysts encompassing supported metals, metal oxides and modified zeolites exchanged with transition or alkali-earth metals were tested for cyclohexane oxidation. The magnesium vanadate, vanadium-magnesium mixed oxides and neodymium- and samarium vanadate catalysts were found as appropriate catalysts for the oxidehydrogenation of cyclohexane to cyclohexene. Remarcable results were obtained recently by using nickel supported catalysts on non porous microparticulate alumina, or over egg-

shell catalysts manufactured by anodic oxidation where the active component was again nickel oxide. The activity and selectivity of these catalysts was attributed to the formation on the carrier surface of a bi-dimensionally interlaced nickel oxide monolayer, a species that preserves the oxidative characteristics of the p-type semiconductors but prevents their amplification due to the presence of the bulk phase.

The mechanism of the oxidative generation of cyclohexane to cyclohexene depends on the catalyst nature and on the temperature, the extraction of the hydrogen atoms being achieved either by electrophilic (at lower temperatures) or by nucleophilic (at higher temperatures) oxygen species. The kinetics of cyclohexane oxidation depends here on the nature of the catalyst and the reaction conditions, but is generally accepted that the rate-determining step is the the heterolytic or homolytic dissociation of the first C–H bond. The catalytic oxidation of cyclohexane begins as a parallel reaction network from cyclohexane to cyclohexene and carbon oxides, and continues with successive transformation of cyclohexene to cyclohexadiene and benzene. To achieve high cyclohexene selectivity catalysts are needed, which are able to suppress the non-selective transformation of cyclohexane to inorganic products and to desorb cyclohexene rapidly. Further researches in these directions are still required.

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