Inhibition effects in the partial oxidation of cyclohexane on polymer supported Co(II) catalysts

DAVOR LONČAREVIĆ, ŽELJKO ČUPIĆ[*,#] and MAJA ODOVIĆ

Institute of Chemistry, Technology and Metallurgy, Department of Catalysis and Chemical Engineering, Njegoševa 12, 11000 Belgrade, Serbia and Montenegro (e-mail: zcupic@nanosys.ihtm.bg.ac.yu)

Abstract: Polymer supported catalysts with different contents of metal ions where synthesized by wet impregnation of the degassed support from ethanolic solutions of cobalt(II) nitrate. A macroreticular copolymer of poly-4-vinylpyridine with divinyl-benzene was used as the support. The prepared catalysts were tested in the partial oxidation of cyclohexane to cyclohexanol and cyclohexanone. Activity tests were performed in a stainless steel, laboratory scale, stirred autoclave, in the semi batch regime under isothermal and non-isothermal conditions. Isothermal experiments where performed at 170 °C for 120 min. In the non-isothermal conditions. isothermal experiments where performed at 170 °C for 120 min. In the non-isothermal experiments, a constant heating rate of 0.3 degree/min was used in the range between 110 °C and 170 °C. Non-linear, least-squares analysis with the simplex optimization method and numerical simulation of the reaction model in each iterative step was used for the kinetic characterization of the process in a non-stationary, semi-batch regime. Apparent rate constants were obtained as an invariant measure of the catalytic system. A non-linear effect of the content of metal ions on the reaction rate and on the ratio of the yield of the products was observed, which is attributed to a complex interactions between the reaction medium and the heterogeneous catalyst, including a catalyst-inhibition effect.

Keywords: cyclohexane oxidation, polymer supported catalysts, reaction kinetics.

INTRODUCTION

The partial oxidation of cyclohexane (CH) to a mixture of cyclohexanol (CHL) and cyclohexanone (CHN) is an important homogeneous catalytic industrial process in which a soluble cobalt catalyst is used. Also, some quantity of cyclohexyl hydroperoxide (CHHP) is usually obtained, as a precursor of the main products CHL and CHN. The process is usually stopped at conversion values of

---

*   Corresponding author.
\#   Serbian Chemical Society active member.

3–8 mol%, and selectivities of 70–80 mol% with a CHL/CHN ratio higher than one. If the process were allowed to proceed to higher conversion levels, large amounts of various byproducts would be obtained. Among the byproducts, mono- and di-carboxylic acids are the most important (adipic, valeric and succinic acid). To a certain extent, the deep oxidation products CO and CO_2 are usually also obtained.[1]

There is general agreement in the literature that cyclohexane is oxidized in a radical-initiated reaction.[2–4] Recent kinetic and thermochemical analyses of the catalytic oxidation of lower alkanes confirmed that the formation of free alkyl radicals is the most energetically feasible process of activation of the initial molecule.[5] The reaction kinetics of CH oxidation depend not only on the mechanism of the heterogeneously or homogeneously catalyzed reaction, but also on the influence of the reactor walls, the mechanism of the uncatalyzed thermal oxidation process and mass transport limitations.

Mass transport of oxygen can sometimes be the limiting process for rate of CH oxidation, especially in large industrial reactors. Therefore, special attention must be given to mixing. Various reactor were designed to avoid this limitation in industrial applications.[4] Under laboratory conditions adequate mixing can be easily achieved.

At temperatures higher than 150 °C, the oxidation of cyclohexane also occurs as a thermal, non-catalytic process.[3] The mechanism of the non-catalytic oxidation of cyclohexane is important since it also contributes significantly to the catalytic process. The reaction scheme of Kharkova with 19 reactions[3] was reported to give a good correlation with experiments. The application of this model is limited to conversion levels lower than 8 %. On the other hand, smaller models were used to explain the experimental results for particular reaction conditions, with a similar accuracy.[4] It was accepted in these simplified models that CHL and CHN are produced from CHHP through independent pathways, but also that CHL is further oxidized to CHN, which is further oxidized to the deep oxidation products.

Several authors investigated the influence of the reactor walls on the reaction kinetics of cyclohexane oxidation.[2,6] When the reaction was performed in a glass reactor or a passivated one a significant amount of CHHP was obtained. However, when a stainless steel reactor was used, decomposition of the CHHP occurred to a significant extent and the main products where CHL and CHN.[6]

The catalyst could not only have some impact on the initiation phase of the process, but also on the propagation stage. Several reactions have been proposed to explain the role of the catalyst in the oxidation of CH, but only the principal pathways are important for the global kinetics of the oxidation. The role of a catalyst is sometimes introduced into a model of the uncatalyzed reaction through the contribution of particular pathways to the value of the rate constants. Hence, for the catalytic oxidation of CH, models of the non-catalytic process were used with adjusted rate constants. A model of this type has already shown good results in the characterization of the process.[4]

The amount of the active metal in the reaction zone seems to be critical for the proper behavior of the reaction system. If the amount of Co is too low, a significant fraction of CHHP is formed. On the other hand, if the amount of Co is too high, adipic acid and a lot of other byproducts are obtained. Moreover, it was noted earlier that if the amount of Co in the reaction system is higher than the amount of CHHP produced, the catalyst could have an inhibition effect due to peroxo complex formation.[1] This process removes CHHP from the reaction, competing in this way with chain propagation reactions and, therefore, leading to a decrease in the oxidation rate.

A significant number of recent investigations into cyclohexane oxidation was focused on the heterogenation of batch reactions, which should afford an easily recoverable catalyst having a reactivity similar to its initial value with the possibility of adaptation to fixed and fluid beds.[7,8] The kinetics of CH oxidation on a heterogeneous catalyst is a complex problem, for which no completely satisfying explanation exists yet. In some cases intriguing non-linear effects are observed, including periodic oscillations in the reaction rates.[7] It was reported that some heterogeneous catalysts could favor the formation of CHN over CHL.[9] An important contribution of heterogeneous catalysts to the patways of the free radical chain mechanism was confirmed by Sinev who claimed that "the overall reaction network includes both homogeneous and heterogeneous elementary reactions of primary and secondary free radicals".[5]

A high preference for the formation of CHL and CHN with usual conversion levels in the oxidation of CH was achieved with polymer supported Co catalysts.[10,11] There was no leaching detected despite the fact that leaching is known to be the biggest problem in the application of heterogeneous polymer supported catalysts generally. However, the activity of the polymer supported catalysts changed during the oxidation process and on reuse of the catalyst samples, the oxidation rates were lower, but the product ratio was retained at a level typical for a catalytic process rather than for a non-catalytic one, evidencing a modified catalytic activity in the second cycle.[12]

In the present study, the effects of catalyst-inhibition on the kinetics of CH oxidation on polymer supported Co(II) catalysts were analyzed, and the chosen model of the process was fitted to the experimental results. For the modeling of the reaction kinetics, the small model of Alagy was the most appropriate among several simple models, because it includes only the most important reaction species monitored in our kinetic experiments. This property gave the possibility of comparing the model with the experiments in the most appropriate way.

EXPERIMENTAL

Catalyst preparation

Catalysts where synthesized by wet impregnation of the degassed support with ethanolic cobalt(II) nitrate solutions. A macroreticular copolymer of poly-4-vinylpyridine with divinyl-

benzene P4PV-DVB (REILLEX-425, produced by Reilly Tarr & Chemical Corporation), was used as the support.[8,13] The used polymer support was thermally stable below 240 °C, in air. 10 g samples of P4VP-DVB were immersed in 100 ml or ethanolic cobalt(II) nitrate solution. After stirring for 3 h at 20 °C, the solid P4VP-DVB-Co^{2+} was filtered and washed. The solid powder was dried at 140 °C for 24 h. The content of Co^{2+} on the polymer samples was determined indirectly by measuring polarographically the amount of Co^{2+} in the residual ethanolic solution (A0 – 0.11 mass%, A1 – 0.52 mass %, A2 – 1.39 mass %, A3 – 3.08 mass %, and A4 – 5.72 mass %). Under employed preparation conditions, the formation of coordination bonds between Co and the pyridine rings of the polymer suport was to be expected.[8]

Activity measurement

Activity tests were performed in a stainless steel, laboratory scale (100 cm^3), stirred autoclave, with precise control of the temperature and of the stirring speed, produced by Autoclave Engineers. In all experiments the following conditions were used: air pressure 2.8 MPa, stirrer speed 350 rpm, and the air flow rate was maintained at about 100 cm^3 min^{-1}. The reactor was in a semi-batch regime, since the liquid substrate (CH) and polymer supported catalyst were charged at the beginning, but the oxidizer (air) was continuously supplied during the reaction. The composition of the liquid phase was analyzed by gas chromatography using a stainless steel column packed with 10 % Carbowax 20M on Chromosorb WAW, coupled to a flame ionisation detector. The composition of the gas phase was analyzed by gas chromatography using Hayesep D and Molecular Sieve 5A packed columns with a TCD detector.

Activity tests were performed under isothermal and non-isothermal, (temperature programmed oxidation – TPO) conditions. The isothermal experiments were performed at 170 °C temperature for 120 min. In the non-isothermal, TPO experiments, after an initial fast heating up to 110 °C, the temperature was increased to 170 °C at a constant heating rate of 0.3 degree/min, and then mantained at 170 °C for 10 min before the reaction was stopped. Several samples were analyzed in this time/temperature interval.

In the blank experiment, the reactor described above was charged with 75 cm^3 of cyclohexane only, to estimate the influence of the reactor walls. In all the catalytic tests the reactor was charged with an additional 1.5 g of a catalysts sample. Samples with different contents of Co were used.

It was considered that the mixing was fast enough for the system to be in the kinetic regime, which was confirmed in several tests at different mixing rates in the interval 150–450 rpm. There was almost no difference in the yields of CHL and CHN when the mixing rate was varied in this wide range. Good mixing was very important for this system not only to avoid diffusion problems, but also to obtain a fast dissolution of oxygen in the liquid CH. The autoclave reactor used in these experiments was particularly well equipped for gas–liquid reactions, since mixing was used to improve the contact between the two phases by convection.

In the leaching test, the catalyst and the liquid phase were separated at the end of the oxidation experiments and after digestion the liquid phase was analyzed. DP polarography and stripping voltammetry were performed with the use of a computer controlled instrumental set-up and an instrument model 757 VA Computrace (Metrohm). The leaching of cobalt was estimated to be less than 0.2 %, relative to the initial amount of cobalt.

Numerical procedure

As it was noted before, the reactor was operated in a non-stationary, semi-batch regime. Therefore, a numerical procedure was necessary for kinetic characterization of the preocess.

Non-linear, least-squares analysis with the simplex optimization method[15] was used to evaluate the optimal values of the rate constants for each kinetic test. In every step of the iterative optimization procedure, the numerical simulation was performed with the Gear algorithm[16] and the simulated concentrations were compared with the experimental ones in both the liquid and gas phase. The coupled rate constants were evaluated simultaneously,[17] from dimensionless forms of the dif-

ferential equations, obtained from parametrization of the Stoichiometric Network Analysis.[18] The sequence at which the rate constants where evaluated was determined from mathematical analysis of the kinetic model. The procedure is explained in more details in the Appendix.

For evaluation of the rate constants, the model shown in Fig. 1 was obtained by simple modification of the Alagy's small model.[4] Only the last reaction in the original Alagy model was modified. Particularly, it was divided into the contributions of two independent pathways leading to CO or to CO_2 as the final product because the experimental results enabled the determination of the formal kinetic parameters of both pathways.
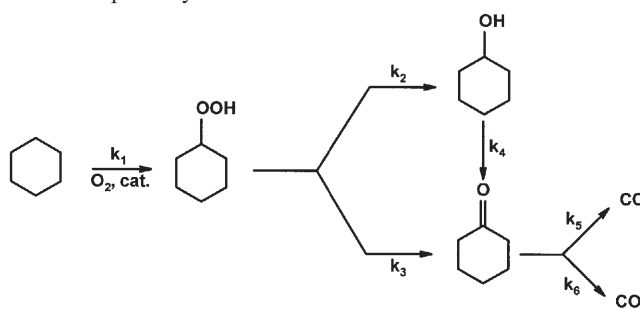

Fig. 1. The model of CH oxidation, used for the kinetics investigation.

In the model (Fig. 1) only the rates of the deep oxidation reactions 5 and 6 are dependent on the oxygen concentration. This is the way to model the fact that reactions 5 and 6 are the most sensitive to the oxygen concentration, since several molecules of oxygen are needed for the oxidation of each molecule of CHN. Actually, the influence of the oxygen concentration on the oxidation rate is limited by the fact that oxygen has first to be dissolved in the CH before it can react. The concentration of the dissolved oxygen is limited by the solubility constant and is approximately constant during the process.[4]

The role of the catalyst is introduced into the model through the contribution of the catalytic reactions to the overall reaction rate of the pathways which constitute the model in Fig. 1. Therefore, the catalysts were characterized here by the evaluation of the optimal rate constants of the model, according to the experimental results. This approach gives a general picture of the catalyst activity and selectivity. However, it must be remembered that the obtained rate constants are only apparent ones.

RESULTS AND DISCUSSION

The concentrations of the main products in the liquid phase samples of the non-isothermal oxidations are presented in Fig. 2, for CH oxidation in the blank reactor (BE), with polymer support (PVP) and with catalysts A0 and A4 (the samples with the lowest and highest contents of Co, respectively). It can be seen that the polymer-supported catalysts decreased the initial temperature of the oxidation process (Fig. 2) in comparison with the blank reactor. On the other hand, the polymer support itself influenced the reaction system in the opposite direction *i.e.*, when polymer was present in the system without Co, the reaction started at even higher temperatures, probably due to the removal of free radical species from the solution, which is the usual effect of aromatic functionalities, sach as pyridine rings[19] from the PVP-DVB support. Moreover, it was observed that the oxidation rate increased with increasing concentration of the Co on the polymer. In combination with the results of the leaching tests (the leaching of cobalt was estimated to be less than 0.2
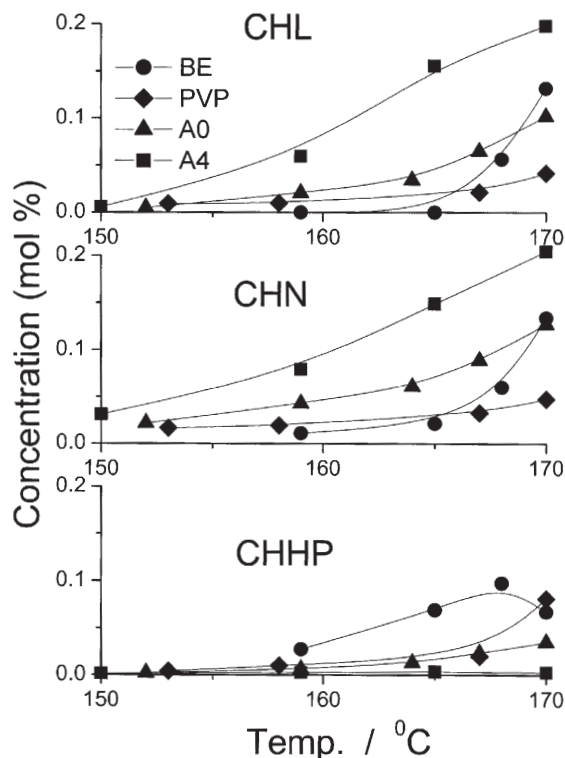
Fig. 2. Concentrations of the main products in the liquid phase samples from the non-isothermal experiments, for CH oxidation in the blank reactor (BE), with polymer support (PVP) and with catalysts A0 – 0.11 mass %, and A4 – 5.72 mass % (the one with lowest and the one with highest content of Co). Experimental values are represented by symbols.

%, relative to the initial amount of cobalt), it was clearly proved that the supported Co ions were catalytically active during the cyclohexane oxidation. Obtained results at lower temperature values imply that prepared catalysts could be used for the CH oxidation at temperature lower then 160 °C, with considerable activity.

The concentrations of the main products in both the gas (CO and CO_2) and the liquid (CHL and CHN) phase samples, from the isothermal experiments (170 °C) are presented in Fig. 3, for CH oxidation in the blank experiment (BE), and with catalyst samples having different contents of Co. At 170 °C, a significant conversion was obtained in the blank reactor, without catalyst (Fig. 3, BE). This uncatalyzed reaction partially covers the catalytic one. Probably the reaction on the reactor walls occurs, as was to be expected in a stainless steel reactor. The main products were cyclohexanol and cyclohexanone. Cyclohexylhydroperoxide was initially formed in significant amounts, but it actually passed through a maximum with reaction time and slowly disappeared there after. In addition, significant amounts of CO and CO_2 were detected.

Nevertheless, in catalytic experiments at 170 °C (Fig. 3, A0, A1, A2, A3 and A4) several changes were observed in comparison to the blank experiment (Fig. 3, BE). The main difference was that CHHP was almost completely decomposed in most of the catalytic systems. Only in the test with the catalyst A0, the one with the
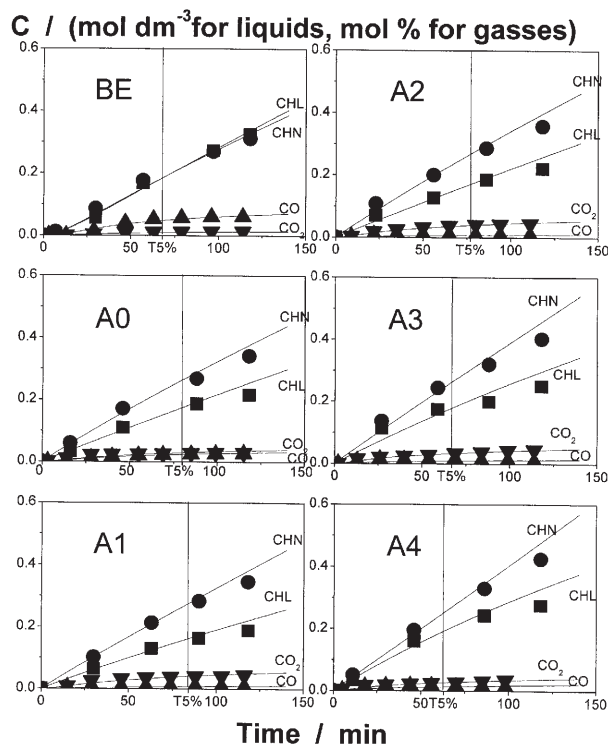
Fig. 3. The concentrations of the main products in both gas and liquid phase samples, from the isothermal experiment (at 170 °C) for CH oxidation in the blank reactor (BE), and with a catalyst samples with different contents of Co (A0 – 0.11 mass %, A1 – 0.52 mass %, A2 – 1.39 mass %, A3 = 3.08 mass % and A4 – 5.72 mass %). The experimental values are represented by symbols and the numerical simulation by lines. The time corresponding to 5 % conversion is indicated in each diagram.

lowest Co content, was a significant concentration of CHHP measured during the initial phase of the reaction. Moreover, in all of the catalytic systems, the yields of CHL and CO decreased while the yields of CHN and CO_2 increased in comparison to the blank experiment. The described complex changes in the reaction kinetics, being dependent on the reaction conditions and time, had to be characterized through some invariant measure, such as the rate constant.

TABLE I. Rate constants of the model in Fig. 1, obtained from the kinetic tests at 170 °C, with polymer supported Co catalysts with different amounts of Co. (BE – blank experiment, A0 – 0.11 mass %, A1 – 0.52 mass %, A2 – 1.39 mass %, A3 = 3.08 mass % and A4 – 5.72 mass %)

Co/wt.%	k_1/s^{-1}	k_2/s^{-1}	k_3/s^{-1}	k_4/s^{-1}	k_5/dm^3 mol^{-1} s^{-1}	k_6/dm^3 mol^{-1} s^{-1}
5.72	1.36×10^{-5}	1.18×10^{0}	1.42×10^{0}	4.41×10^{-5}	2.66×10^{-4}	5.20×10^{-4}
3.08	1.27×10^{-5}	2.18×10^{0}	3.14×10^{0}	2.61×10^{-5}	1.63×10^{-4}	5.75×10^{-4}
1.39	1.10×10^{-5}	6.59×10^{0}	1.11×10^{1}	3.32×10^{-11}	1.01×10^{-4}	5.29×10^{-4}
0.52	1.02×10^{-5}	3.01×10^{0}	5.12×10^{0}	2.00×10^{-5}	8.93×10^{-5}	4.67×10^{-4}
0.11	1.07×10^{-5}	1.81×10^{1}	3.00×10^{1}	4.48×10^{-9}	3.06×10^{-4}	3.72×10^{-4}
0.00	1.25×10^{-5}	7.62×10^{-4}	8.55×10^{-4}	2.91×10^{-11}	1.18×10^{-3}	2.31×10^{-4}

The described numerical procedure was successfully applied in all cases. The obtained rate constants are summarized in Table I and the fitted kinetic curves are

compared with the experimental results in Fig. 3. The most important changes were obtained in the rate constants k_2 and k_3, which were several orders of magnitude higher in the catalytic system, than in the blank reactor. Nonlinear dependencies of the rate constants k_1 and k_5 on the Co concentration on polymer were observed, with a noteworthy minimum for the sample A1. Furthermore, the rate constant k_6 first increased with increasing Co content and then remained a nearly constant at the higher Co contents.

On the other hand, it seems that the obtained variations in k_4 were caused by the numerical procedure rather than by the chemical process itself. The procedure converged to fairly low values of k_4 and it turned out that the system was not sensitive to a particular value of this parameter. Therefore, the obtained values for k_4 varied by several orders of magnitude, without having a significant effect on the reaction kinetics and without any correlation with the amount of Co on the support.

It was considered that the achieved approximate agreement between the levels of the product concentrations in the experiment and the simulation (symbols and lines in Fig. 3, respectively) was sufficient for the evaluation of the relative trends in the changes in the conversion and selectivity. Therefore, the numerical simulation with the obtained rate constants was further used to determine the set of process parameters in Table II. The conversion level of about 5 % was chosen for the comparison between the reaction systems. Several properties were analyzed: $T_{5\%}$ (duration period needed for the achievement of 5 % conversion) S_{KA} (selectivity toward ketone and alcohol only, at 5 % conversion), S_{KAP} (selectivity toward hydroperoxide, ketone and alcohol, at 5 % conversion), K/A ratio the in liquid phase (ratio between the concentration of ketone and alcohol, at 5 % conversion) and the CO/CO_2 ratio in the gas phase (at 5 % conversion).

TABLE II. Several process parameters of the reaction systems with polymer supported Co catalysts with different amount of Co: $T_{5\%}$ (duration period needed for the 5 % conversion level to be achieved), S_{KA} (selectivity toward ketone and alcohol only), S_{KAP} (selectivity toward CHHP, CHN and CHL), K/A ratio in liquid phase (ratio between ketone and alcohol concentrations) and $[CO]/[CO_2]$ ratio in gas phase.

Co/wt %	$T_{5\%}$/min	S_{KA}	S_{KAP}	[CHL]/[CHN]	$[CO]/[CO_2]$
5.72	63	0.965	0.965	0.764	0.515
3.08	67	0.961	0.961	0.681	0.286
1.39	77	0.954	0.954	0.638	0.193
0.52	84	0.950	0.950	0.589	0.194
0.11	80	0.947	0.947	0.662	0.823
0.00	68	0.804	0.953	0.996	5.034

For almost all the catalyst samples (except for the sample A4 with the highest Co content), at 170 °C, the oxidation rate was lower than in the blank experiment

(the values of $T_{5\%}$ in Table II were higher). The $T_{5\%}$ conversion periods were directly correlated with the value of k_1. The minimum in the k_1 values corresponds to the maximum in the $T_{5\%}$ values and, accordingly, to the minimum in the oxidation rate. This catalyst-inhibition effect is most significant for the A1 sample with 0.52 wt.% Co.

Moreover, at the 5 % conversion level, the selectivity (S_{KAP}) to the formation of a mixture of useful products, CHHP, CHL and CHN is practically unchanged by the presence of the catalyst. Hence, there was no change in the ratio of the partial to the deep oxidation. The principal contribution of the catalyst was that CHHP was almost completely decomposed in most of the catalytic systems (also in accordance with the rate constant k_2 and k_3 in Table I), except in the system with the lowest Co content. Only the catalyst samlpes with a higher Co content (than 0.52 wt.%) were also somewhat active in the initiation part of the process, which was observed through the increase of k_1 and the decrease of $T_{5\%}$.

In the present experiments, the CO/CO_2 ratio also changed with the presence of the catalyst, and this change was in correlation with the change of the CHL/CHN ratio. A particularly interesting fact was that the maximum in $T_{5\%}$ correlated with the minimum in the CHL/CHN ratio and in the CO/CO_2 ratio (Table II). Hence, a reaction pathway probably exists in the catalytic system, which connects production of the CHL and CO on one hand, and the production of CHN and CO_2 on the other. The correlation between the $T_{5\%}$ values and the product ratios would also mean that the two different pathways have opposite influences on the rate of the overall CH oxidation. A more detailed model of the reaction mechanism would be needed to describe these observed properties and the reaction pathways.

The obtained differences in the product ratios means that the reaction mechanism of CHHP decomposition was changed in the catalytic system. The reaction mechanism of the deep oxidation is very important for the design strategy in order to achieve improvements in the process selectivity. However, there is not much information on this part of the reaction mechanism in the literature. CO formation was generally expected from the aldehyde groups (and/or corresponding radicals) in the byproducts of CHN over-oxidation. On the other hand, CO_2 formation was expected from the carboxyl groups.

At low conversion values, the reaction rate of the uncatalyzed CH oxidation (blank experiment) is kinetically controlled by the steady state reaction rates of CHHP formation and decomposition. The uncatalyzed reaction was probably inhibited by the catalyst through the formation of peroxo complexes with Co.[1] This process removes CHHP from the reaction mixture, completing in this way with the reactions of chain propagation, and therefore leading to a decrease in the oxidation rate. This pathway, which also leads to a lower cyclohexanol to cyclohexanone ratio, may be connected with the dehydration of cyclohexyl hydroperoxide on the polymer supported catalysts to cyclohexanone and water, as opposed to the free-radical decomposition mechanism of cobalt and of the uncatalyzed reaction.

Therefore, the overall oxidation rate is decreased when a low Co content (below 0.52 wt.%) is used.

The increased amount of the Co above 0.52 wt.% contributes by adding an excess of unoccupied Co, possibly active in the initiation part of the process.

Hence, increasing the Co content on the polymer up to 0.52 wt.% leads to an increase in the contribution of the reaction pathway corresponding to CHN and CO_2 production, and a decrease of the reaction pathway corresponding to CHL and CO production. At higher values of Co content (higher than 0.52 wt.%) the contributions of the both pathways rates were increased.

CONCLUSION

A numerical procedure for the kinetic characterization of the catalytic system was successfully applied. Apparent rate constants were obtained as an invariant measure of the catalytic system.

The initiation temperature of the oxidation process decreased in the presence of polymer supported Co, giving evidence of catalytic activity.

The influence of the Co concentration on the reaction kinetics at 170 °C was strongly nonlinear. The increased CHHP decomposition rate was followed by inhibition of CHHP formation, resulting in a decreased oxidation rate for almost all the tested catalyst samples.

The selectivity to "peroxide, alcohol, ketone mixture" at 5 % conversion level was unchanged in the catalytic systems, and therefore the ratio between the deep and partial oxidation was the same, but the product ratios differed from those in the blank experiment.

The CO/CO_2 ratio also changed in the presence of the catalyst, and this change was in correlation with the changes in the other product ratio, indicating new reaction pathways which connect CHL and CO production on the one hand, and CHN and CO_2 production on the other.

ИЗВОД

ЕФЕКТИ ИНХИБИЦИЈЕ У ПАРЦИЈАЛНОЈ ОКСИДАЦИЈИ ЦИКЛОХЕКСАНА Co(II) КАТАЛИЗАТОРИМА НАНЕТИМ НА ПОЛИМЕРНИ НОСАЧ

ДАВОР ЛОНЧАРЕВИЋ, ЖЕЉКО ЧУПИЋ и МАЈА ОДОВИЋ

Инсшишуш за хемију, шехнолоґију и мешалурґију, Ценшар за кашализу и хемијско инжењерсшво, Њеґошева 12, 11000 Беоґрад

Катализатори на полимерном носачу, са различитим садржајем металних јона, синтетисани су импрегнацијом дегазираног носача из алкохолног раствора кобалт(II) нитрата. Макроретикуларни кополимер поли-4-винилприридина са дивинилбензеном

је коришћен као носач. Припремљени катализатори су тестирани у реакцији парцијалне оксидације циклохексана до смеше циклохексанола и циклохексанона. Каталитички тестови су изведени у лабораторијском, аутоклаву од нерђајућег челика, под изотермалним и неизотермалним условима. Изотермални експерименти су извођени на 170 °C током 120 min. У неизотермалним експериментима коришћена је константна брзина грејања од 0,3 °C/min, у интервалу 110 – 170 °C. Нелинеарна анализа најмањих квадрата са симплекс методом оптимизације у нумеричком симулацијом у сваком итерационом кораку, је коришћена за кинетичку карактеризацију процеса у нестационарном режиму. Добијене су привидне константе брзине као инваријантна карактеристика каталитичког система. Уочени су нелинеарни ефекти садржаја металних јона на брзине реакција и на односе концентрација производа. Ови ефекти су приписани сложеној интеракцији реакционе средине и хетерогеног катализатора, која укључује и инхибицију.

REFERENCES

1. *Ullmann's Encyclopedia of Industrial Chemistry*, Verlag Chemie, Weinheim, 1975, p. 680
2. I. V. Berezin, E. T. Denisov, N. M. Emanuel, *The Oxidation of Cyclohexane*, Pergamon Press, New York, 1969, p. 274
3. T. V. Khar'kova, I. L. Arest-Yakubovich, V. V. Lipes, *Kinetika i Kataliz* **30** (1989) 954
4. R. Pohorecki, J. Baldyga, W. Moniuk, W. Podgorska, A. Zdrojkowski, P. T. Wierzchowski, *Chem. Eng. Sci.* **56** (2001) 1285
5. M. Y. Sinev, *J. Catal.* **216** (2003) 468
6. U. Shuchardt, W. A. Carvalho, E. V. Spinace, *Synlett* **10** (1993) 713
7. D. C. Sherrington, *Pure & Appl. Chem.* **60** (1988) 401
8. G. L. Goe, C. R. Marston, E. F. V. Scriven, E. E. Sowers in *Catalysis of Organic Reactions*, D. W. Blackburn, Ed., Marcel Dekker, Inc., New York, 1989, p. 275
9. J. D. Chen, R. A. Sheldon, *J. Catal.* **153** (1995) 1
10. Ž. Čupić, S. Petrović, A. Terlecki-Baričević, *Proceedings of the 9th International Symposium*, Heterogeneous Catalysis, Varna, Bulgaria, 2000, pp 289–294
11. Ž. Čupić, A. Terlecki-Baričević, M. Stanković, *4th World Congress of Oxidation Catalysis*, Berlin, 2001, Ex. Abstracts, pp. 155–158
12. D. Lončarević, Ž. Čupić, A. Terlecki-Baričević, *3rd International Conference of the Chemical Societies of the South-Eastern European Countries*, Bucharest, 2002, Book of Abstracts, p. 281
13. A. Terlecki-Baričević, Ž. Čupić, S. Anić, Lj. Kolar-Anić, S. Mitrovski, S. Ivanović, *J. Serb. Chem. Soc.* **60** (1995) 969
14. G. B. Shul'pin, *J. Mol. Cat. A: Chemical* **189** (2002) 36
15. J. A. Nelder, R. Mead, *Computer J.* **7** (1965) 308
16. C. W. Gear, *Numerical Initial Value Problems in Ordinary Differential Equations*, Prentice Hall, Englewood Cliffs, NJ, 1971
17. F. F. Perez Pla, J. F. Bea Redon, R. Valero, *Chemom. Intell. Lab. Syst.* **53** (2000) 1
18. B. L. Clarke, *Cell Byopohysics* **12** (1988) 237
19. D. H. R. Barton, *J. Mol. Cat. A: Chemical* **117** (1997) 3.

APPENDIX

The expressions for the rate equations in the used model (Fig. 1), are given by:

$$\frac{d[CH]}{dt} = -k_1[CH] \tag{1}$$

$$\frac{d[CHHP]}{dt} = k_1[CH] - k_2[CHHP] - k_3[CHHP] \tag{2}$$

$$\frac{d[CHL]}{dt} = k_2[CHHP] - k_4[CHL] \tag{3}$$

$$\frac{d[CHN]}{dt} = k_3[CHHP] + k_4[CHL] - k_5[CHN] \cdot [O_2] - k_6[CHN] \cdot [O_2] \tag{4}$$

$$\frac{d[CO]}{dt} = k_5[CHN] \cdot [O_2] - F \cdot [CO] \tag{5}$$

$$\frac{d[CO]}{dt} = k_6[CHN] \cdot [O_2] - F \cdot [CO_2] \tag{6}$$

where $[O_2]$ means mols of oxygen in the gas phase divided by the CH volume and F is the flux of air through the reactor in the parts of the gas phase volume per unit time.

The rate constants could not be evaluated. Therefore, it was necessary to evaluate the coupled rate constants simultaneously.[17]

Hence, significant decoupling of the kinetic parameters and computation savings were obtained when the differential Eqs. (1)–(6) were expressed in dimensionless form. The parametrization from the Stoichiometric Network Analysis was used here to obtain the dimensionless form of the differential equations[18]:

$$\dot{C} = -C \tag{7}$$

$$\dot{P} = \frac{k_2 + k_3}{k_1} \cdot (C - P) = \alpha \cdot (C - P) \tag{8}$$

$$\dot{L} = \frac{k_4}{k_1} \cdot (P - L) = \beta \cdot (P - L) \tag{9}$$

$$\dot{N} = \frac{k_5 + k_6}{k_1} \left[\left(1 - \frac{k_2}{k_2 + k_3} \right) P + \frac{k_2}{k_2 + k_3} L - N \right] = \gamma \cdot [(1 - \delta)P + \delta L - N] \tag{10}$$

where $C = [CH]/[CH]_0$, ($[CH]_0$ is the initial value of the cyclohexane concentration), $P = [CHHP]/[CHHP]_{ss}$, $L = [CHL]/[CHL]_{ss}$, $N = [CHN]/[CHN]_{ss}$, and subscript "ss" stands for the steady state approximation over the intermediary species CHHP, CHL and CHN resulted in the formulas for the steady state concentrations

$$[CHHP]_{ss} = \frac{k_1}{k_2 + k_3}[CH]_0 \tag{11}$$

$$[CHL]_{ss} = \frac{k_2}{k_4}\frac{k_1}{k_2 + k_3}[CH]_0 \tag{12}$$

$$[CHN]_{ss} = \frac{k_1}{k_5 + k_6}[CH]_0 \tag{13}$$

The concentrations were normalized to steady state values and the time was also normalized to the rate of the reaction 1 of the model (Fig. 1). The rate constants are related with dimensionless parameters through:

$$k_1 = \tau/t \tag{14}$$

$$k_2 + k_3 = \alpha k_1 \tag{15}$$

$$k_4 = \beta k_1 \tag{16}$$

$$k_3/k_2 = \frac{1}{\delta} - 1 \tag{17}$$

$$k_5 + k_6 = \gamma k_1 \tag{18}$$

While the rate constant k_1 would be easy to obtain even from classical reaction kinetics, the other rate constants appear to be grouped in dimensionless parameters. However, the dimensionless parameters are almost completely decoupled in the dimensionless differential Eqs. (7)–(10). On the other hand, the dimensionless form of the differential equations is not convenient for the direct estimation of the parameters. Therefore, we have to express the relation between the dimensionless variables and the concentrations explicitly.

$$[CH] = [CH]_0 \cdot C \tag{19}$$

$$[CHHP] = \frac{\delta[CH]_0}{\alpha} \cdot P \tag{20}$$

$$[CHL] = \frac{\delta[CH]_0}{\beta} \cdot L \tag{21}$$

$$[CHN] = \frac{[CH]_0}{\gamma} \cdot N \tag{22}$$

For the evaluation of k_1 Eq. (7) has to be integrated only once, and (since $[CH]_0$ is known) k_1 as actually evaluated by optimization of the algebraic time-scaling Eq. (20) with the appropriate minimization criteria corresponding to the difference between the experimental $[CH](t)$ and the simulted $C(\tau)$ values.

In the next step, a was evaluated from differential Eq. (8). It was not possible to measure [CHHP] experimentaly with a satisfying accuracy. Therefore, the value of the CHHP decomposed, obtained from the numerical simulation was compared with the sum of all of its products measured.

Further, from Eq. (21), it can be seen that the constants b and d are coupled and so have to be evaluated simultaneously. The significant advantage of the proposed approach is that for each estimated value of b, only one integration of the differential Eq. (9), is preformed and then the optimal value of δ is found from the algebraic Eq. (21). CHL was used for the minimization criterion in this step.

From the Eq. (10) the parameter γ was simply evaluated with the value of CHN used for the minimization criterion. Finally, the rate constants were evaluated from the Eqs. (14)–(28). The evaluation of the separate values for the k_5 and k_6 from the original differential equations (5) and (6) for CO and CO_2 was then an easy task.