Polish J. of Environ. Stud. Vol. 17, No. 6 (2008), 887-893

Original Research

Hydrodechlorination of Chloroaromatic Compounds over Carbon-Supported Ni-Mo Catalysts

A. Klijanienko, G. Gryglewicz, M. Stolarski, S. Gryglewicz*

Department of Chemistry, Wrocław University of Technology, 50-344 Wrocław, Gdańska 7/9, Poland

Received: 1 December, 2007
Accepted: 30 July, 2008

Abstract

The hydrodechlorination (HDCl) process of 2-chlorodiphenyl, 4-chlorodiphenyl, chlorobenzene, chloronaphthalene and chloroanthracene was studied over a sulphided carbon-supported Ni-Mo catalyst (15 wt% MoO_3, 5 wt% NiO) in a stirred autoclave at 260ºC and at a hydrogen pressure of 3 MPa. Activated carbons of different porosity characteristics were used as Ni-Mo catalyst support. A high chlorine removal for chloroorganic compounds was obtained in the presence of Ni-Mo/C catalysts, ranging from 73 to 99%. For monochlorodiphenyls, the HDCl degree is related to the position of the substituted chlorine atom. 4-chlorodiphenyl was converted to diphenyl to a higher extent compared with 2-chlorodiphenyl. Chloronaphthalene and chloroanthracene were shown to be more susceptible to chlorine removal than chlorobenzene. For comparison, chlorocyclohexane was tested in the HDCl reaction. The dechlorination of chlorocyclohexane proceeded at a much lower temperature compared to chlorobenzene.

Keywords: activated carbon, Ni-Mo catalyst, chloroaromatic compounds, hydrodechlorination

Introduction

Chloroorganic compounds are generally considered a priority pollutant due to their widespread presence in the environment. The chemical industry still continues to produce different groups of halogenated organic compounds constituting undesirable waste or by-products. Most attention has been paid to chlorinated aromatic compounds harmful to living organisms that tend to accumulate in the natural environment [1].

In years past, industrial products containing chloroarenes, in particular polychlorinated biphenyls (PCBs), have been used widely as electroinsulating fluids, hydraulic and lubricating fluids as well as heat exchanger fluids. Despite withdrawal of use and restriction on the production of PCBs, large amounts of these compounds continue to be present in environment, either in use or as waste. Electrotechnical equipment containing PCBs is a constant emission source of these compounds to the environment. Therefore, the quick and safe method of PCB degradation is a subject of broad research. A similar problem arises with chlorine derivatives of benzene and its homologues.

At present, organic waste containing chlorine derivatives are commonly being destroyed by high-temperature incineration due to its universalism, relative technical simplicity and availability of reliable technology. A basic problem is the proven possibility of yielding harmful products including chloroarene derivatives such as polychlorinated dibenzodioxins and polychlorinated dibenzofurans [2-4]. Moreover, in the process of incineration the whole material is irreversibly lost. Although there is a possibility

---

*e-mail: stanislaw.gryglewicz@pwr.wroc.pl of using the energy and hydrochloric acid resulting from burning, this does not affect the economic viability significantly.

Biological treatment is capable of degrading haloorganics but conversion is low and the process requires expensive reactors [5]. However, biological methods are irreplaceable for decontamination of large areas of soils and water reservoirs.

A widely recommended method of dechlorination of chloroorganic compounds, which is environmentally safe, is degradation under reductive conditions. In a reduction process, toxic by-products such as derivatives of dioxins, furans, and phosgene are not produced. The main reaction product is HCl, which can be easily separated.

The dechlorination of organic chlorinated compounds such as chlorinated benzenes and chlorinated phenols using hydrogen as a reducing agent and catalysts containing different active elements: Pd, Pt, Rh and Ni has been widely reported [6, 7]. It is commonly accepted that noble metal catalysts are active at low temperatures, even at room temperature. However, they are easily irreversibly deactivated by hydrochloric acid, which is formed during dechlorination [8].

Catalytic hydrodechlorination (HDCl) is in a certain sense an adaptation of widely applied refinery processes such as hydrodesulphurization, hydrodenitrogenation and hydrodearomatisation. Due to low operating temperature and the recovery of the products, the HDCl process is economically advantageous with respect to incineration [9, 10]. Catalysts with Ni-Mo as an active phase constitute a very efficient system for hydrodechlorination [11]. The main advantages of Ni-Mo catalysts are low price, stability and duration. Such catalysts, when converted to sulphided forms, are characterized by their optimum high activity [12].

A number of supports were tested, including TiO_2, MgO, ZrO_2 and Al_2O_3. A major disadvantage of these materials is that they are susceptible to destruction caused by hydrohalogens. Activated carbon has an advantage over them in this aspect, and is stable in acidic media [13]. In addition, organic compounds, especially arenes, show affinity to polyaromatic carbon surfaces in contrast to mineral supports. A very important aspect from the economy of using precious metal catalysts, especially a highly loaded one, is recovery, refining and recycling of the metal.

The nature of carbon material used as a catalyst support for the HDCl process is also important. It was reported that activated carbon and carbon fibres are suitable for this purpose, but not graphite [8].

In non-catalyzed processes, such as hydrodechlorination of chlorobenzene, the temperature has to be in the range of about 900ºC [14]. Activated carbon alone can already promote the dehalogenation of arene derivatives [15]. Chlorobenzene derivatives are dehalogenated to a high extent below 600ºC, thus, at a temperature lower than needed for the non-catalyzed reaction [16-18]. Therefore, the ability of activated carbon to adsorb especially aromatic compounds can assist in the target dehalogenation process.

It is widely known that catalytic dehalogenation of aromatic compounds is an electrophilic substitution reaction [19, 20]. The fact that 1,2,3,4,5-pentachlorobenzene, in reaction with hydrogen, is first attacked at position *3*, i.e. on the atom of greatest electron density, supports the electrophilic substitution mechanism of hydrodechlorination of chloroaromatics [21]. In the products of the reaction mentioned above, chlorine derivatives with the chlorine atom in position *3* are always absent. Generally, the presence of electron donating substituents (NH_2, CH_3) and electrowithdrawing substituents (Cl, CF_3), as well as their position, affects the hydrodechlorination reaction rate according to the electrophilic mechanism theory [22-24]. However, in some cases the sterical and electronic effects can also overlap. For chlorodiphenyl congeners the chlorine atom in the *-orto* position is the least susceptible to hydrogen substitution [25].

The aim of this work was to evaluate the suitability of activated carbon as a support of Ni-Mo catalyst in the HDCl process of chloroaromatic compounds. Commercial activated carbons and laboratory-prepared activated carbons of different porous structures were tested in this study.

Materials and Methods

Chlorobenzene, chloronaphthalene, chloroanthracene, chlorocyclohexane, heptane, nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$), and ammonium molybdate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$) were purchased from Aldrich (Steinheim, Germany). The commercial-activated carbons CWZ-22 (CG) and Norit SX ULTRA CAT (CN) were obtained from Gryfskand and Norit companies, respectively. 2- and 4-chlorodiphenyls were delivered by Riedel-de Haën The initial concentration of chloroorganic substrates tested was 500 mg/L. Chlorocyclohexane was diluted with heptane. Aromatic chloroorganic compounds were dissolved in heptane with the addition of toluene (10%) to avoid their selective adsorption on the carbon surface of activated carbon. When an aliphatic-aromatic mixture is used as a solvent, this phenomena is not observed (as proven in our work that has not yet been published).

Preparation of Carbon Support

The activated carbon ACP was produced by chemical activation of oak with phosphoric acid. The wood precursor was impregnated with 50% H_3PO_4 solution and subsequently heated to 480ºC at 1ºC min^{-1} in a mixed steam-nitrogen atmosphere. The soaking time was 20 min. The product was washed with distilled water to remove chemicals and dried at 105-110ºC for 2h. ACP1 was obtained by exhausted washing of ACP with distilled water.

Commercial activated carbons CG and CN were pretreated with 5% HCl prior to their use as a support of catalyst.

Table 1. Porous structure characteristics of activated carbons and activated carbon-supported Ni-Mo catalysts.

Carbon support/catalyst	Ash content (wt %)	S_{BET} (m^2/g)	V_{mic} (cm^3/g)	V_{mes} (cm^3/g)	V_t (cm^3/g)	V_{mes}/V_t
CG	0.6	836	0.328	0.160	0.488	0.33
Ni-Mo/CG	-	714	0.294	0.114	0.408	0.28
CN	3.9	1020	0.372	0.437	0.809	0.54
Ni-Mo/CN	-	840	0.355	0.405	0.760	0.53
ACP	9.7	2178	0.800	0.403	1.203	0.33
Ni-Mo/ACP	-	1007	0.377	0.154	0.531	0.29
ACP1	3.3	1718	0.630	0.744	1.374	0.54
Ni-Mo/ACP1	-	1194	0.448	0.457	0.905	0.50

Catalyst Preparation

Ni-Mo catalysts were prepared by incipient wetness technique using activated carbon as a support. Nickel nitrate and ammonium molybdate were used for catalyst loading. Activated carbon was impregnated with molybdenum salt, dried at 105-110ºC and afterwards the sample was heat treated at 300ºC for 3 h in argon atmosphere. Subsequently, the Mo-loaded sample was impregnated with an aqueous solution of Ni salt. After drying, the Mo- and Ni-loaded activated carbon was heat-treated at 400ºC in flowing argon for 3 h. The composition of the active phase was the same for each carbon-supported catalyst, i.e. 5 wt% NiO and 15 wt% MoO_3.

Analyses

The porous structure parameters of the supports and catalysts were determined from nitrogen adsorption and desorption isotherms measured at 77 K with a NOVA 2200 gas sorption analyzer (Quantachrome). The specific surface area (S_{BET}) was calculated using the BET method. The Gurvich rule and Kelvin condensation theory [26], were applied to establish the extent of microporosity (pores with a width < 2 nm) and the pore size distribution of mesopores (pores with a width of 2-50 nm) volume (V_{mes}), respectively. The amount of nitrogen adsorbed at the relative pressure of p/p_0=0.98 was employed to determine the total pore volume (V_t), which corresponds to the sum of the micropore and mesopore volumes. The micropore volume (V_{mic}) was calculated as the difference between total pore volume and mesopore volume. The mesopore fraction was expressed as the ratio of mesopore volume to total pore volume (V_{mes}/V_t).

Scanning electron microscopy with energy dispersive X-ray analysis (Jeol JSM 5800LV, Oxford Link ISIS 300) was applied to monitor the metal distribution and the surface morphology of catalyst.

Hydrodechlorination Process

The HDCl reactions were conducted in microautoclave under hydrogen pressure of 3 MPa at 260ºC for 1 h. 2 ml of substrate solution and 50 mg of catalyst were placed into a reactor in each experiment. Before the HDCl process, the catalyst had been sulphided with 75 µl of diethyl sulphide at 320°C for 45 min. Afterwards the reactor was cooled to the temperature required for the process, and the reaction substrate was injected into the reactor. The reaction mixture was kept homogenous with a magnetic stirrer. After the reaction the reactor was immediately cooled to room temperature. The HDCl degree was determined as an average of two runs.

The reaction products and substrates were analyzed by means of gas chromatography (GC) using a Hewlett Packard HP5890 equipped with a flame-ion detector and column HP-1 (30 m x 0.25 mm ID, 0.25 µm film thickness). A split 1:10 was set and the volume of injected sample was 1 µl. The injector temperature was 280ºC. After injection the oven was heated at 5ºC min^{-1} from 120ºC to a final temperature of 290ºC and held for 10 min. Two independent measurements were performed for each sample. Hexadecane was used as an internal standard for the quantitative analysis.

Results and Discussion

Characteristics of Carbon Supports

Porous structure parameters for carbon supports and Ni-Mo/C catalysts are given in Table 1. The activated carbons used as catalyst support have a well-developed porous structure. They show total pore volume in the range of 0.488-1.374 cm^3/g with the mesopore fraction of 0.33-0.54. The S_{BET} surface area ranges from 836 to 2178 m^2/g. Commercial activated carbons CN and CWZ-22 are characterized by both lower BET surface area and total pore volume, compared to the carbons produced by chemical activation with phosphoric acid (ACP, ACP1). The carbon supports used differ in terms of the amount of inorganic constituents (Table 1). They are characterized by low ash content (0.6-3.9 wt%), except for ACP. An exhausted washing of ACP results in a significant decrease of ash content from 9.7 to 3.3 wt % due to the removal of most phosphorous compounds. This leads to a change in porous structure parameters. An increase in the total and mesopore volumes can be observed, whereas both the BET surface area and the micropore volume are decreased (ACP *vs*. ACP1).

Characteristics of Ni-Mo/C Catalysts

It can be clearly seen that metal loading reduces both the internal surface area and total pore volume, but to different extent depending on the activated carbon used (Table 1). This is accompanied by a decrease in the micropore and mesopore volumes. The largest changes in the porous structure due to metal loading can be observed for ACP with the most developed microporosity among carbon supports used.

The prepared Ni-Mo/C catalysts are characterized by internal surface area from 714 to 1194 m^2/g and total pore volume from 0.408 to 0.905 cm^3/g. For all catalysts the mesopore contribution to the porous structure is lower compared with carbon support.

Fig. 1 shows the comparison of pore volume distribution for Ni-Mo/C catalysts and carbon supports alone. The Ni-Mo/CG and Ni-Mo/ACP catalysts contain mainly micropores, about 70%, reflecting the microporous nature of supports. For Ni-Mo/CN and Ni-Mo/ACP1, the micropores constitute approximately 50% of their total pore volume. It can be seen in Fig. 1 that for all catalysts the contribution of mesopores of different size is similar to that of carbon support used. This means that no preferential blockage of mesopores with a given size range by metal precursors has been occurred. As far as micropores are concerned, a tendency of increasing extent of blockage with micropore volume of carbon support can be observed.

SEM-EDX examination of Ni-Mo/C catalysts prepared by incipient wetness method reveals that nickel and molybdenum are homogeneously distributed on the surface of activated carbon. As an example, Fig. 2 shows these characteristic homogeneous metal dispersions for the Ni-Mo/CN catalyst.

Hydrodechlorination of Monochlorodiphenyls

The results of the catalytic HDCl process carried out on selected monochlorodiphenyls are shown in Table 2. The conversion degree of monochlorodiphenyls to diphenyl in the presence of Ni-Mo/C catalyst is in the range of 71.2-99.1%, whereas for non-catalytic process does not exceed 16%. The lowest chlorine removal is observed for the Ni-Mo/ACP catalyst, which was prepared using activated carbon with high ash content (9.7 wt%). It was found that 4-chlorodiphenyl was distinctly more reactive compared to 2-chlorodiphenyl in the presence of Ni-Mo/C catalysts tested. This fact can be explained by steric reasons. In the case of 2-chlorodiphenyl, the presence of the large phenyl ring placed in the position adjacent to the chlorine atom results in a decrease in the rate of its elimination. For 4-chlorodiphenyl the phenyl group, three bonds away from the chlorine atom, does not hinder the dechlorination reaction.

Table 2. Conversion degree of monochlorodiphenyls during catalytic and non-catalytic HDCl processes (260ºC, hydrogen pressure 3 MPa, reaction time 1 h).

Catalyst	2-chlorodiphenyl	4-chlorodiphenyl
Ni-Mo/CG	85.3	99.0
Ni-Mo/CN	84.7	98.7
Ni-Mo/ACP	71.2	93.7
Ni-Mo/ACP1	86.1	99.1
no catalyst	5.1	15.2

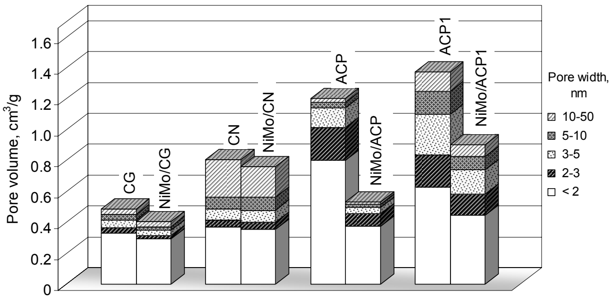

Fig. 1. Pore volume distribution for carbon supports and Ni-Mo/C catalysts.

The obtained results show that the catalytic activity of Ni-Mo/C catalysts does not exhibit any significant correlation with their porous structure. The size of molecules, which were used as substrates in HDCl process, does not exceed 0.5 nm [27]. Therefore, the whole micropore system can be considered as accessible for the substrate molecules. In that case, the activity of the catalyst can be related to the internal surface area. High surface area of the catalyst ensures the availability of the substrate to active phase and in that way favors the progress of the reaction. Moreover, the presence of activated carbon-derived mineral matter can influence the conversion degree in the HDCl reaction. It is well known that some mineral constituents inhibit activity of a catalyst as can be observed, for example, in the case of nickel catalysts [28, 29]. Nickel atoms in the aluminate form can create the undesirable microcrystal phase, which is reduced to a more difficult free metal, being the active phase of the catalyst.

Ni-Mo/ACP shows the lowest catalytic activity among catalysts tested. For 2- and 4-chlorodiphenyl the HDCl

Table 3. Conversion degree of chlorobenzene, chloronaphthalene and chloroanthracene[1)] and chlorocyclohexane[2)] in the catalytic HDCl process.

Catalyst	Chlorobenzene	Chloronaphthalene	Chloroanthracene	Chlorocyclohexane
NiMo/CG	83.0	90.0	97.6	97.7
NiMo/CN	83.2	89.2	98.5	95.5
NiMo/ACP1	85.5	90.0	96.2	94.0

[1)] 260ºC; 3 MPa, 1 h

[2)] 180ºC; 3 MPa, 1 h

degree is 71.2 and 93.7%, respectively. Presumably, it can be explained by an enhanced amount of ACP-derived inorganic constituents in the carbon support (Table 1). A decrease in ash content achieved by exhausted washing of ACP resulted in an increase in the conversion degree of monochlorodiphenyls in the HDCl process. This suggests that phosphorous compounds left after activation of wood play a detrimental role in catalyst activity in the HDCl reaction.

A comparable dechlorination degree of monochlorodiphenyls is achieved for the remaining three Ni-Mo/C catalysts in spite of the fact that they differ in terms of porous structure to a high extent (Table 1). For 2-chlorodiphenyl and 4-chlorodiphenyl, the HDCl degree in the presence of Ni-Mo/CG, Ni-Mo/CN and Ni-Mo/ACP1 is in the range of 84.7-86.1% and 98.7-99.1%, respectively. The ash content in the carbon supports used for the preparation of the above catalysts was between 0.6 and 3.9 wt%.

The results similar to those obtained in our work were reported by Gioia and Murena [11]. In their study decachlorodiphenyl was totally dechlorinated at 300ºC in the presence of an Ni-Mo/Al_2O_3 catalyst.

Hydrodechlorination of Chlorobenzene and Its Homologues

The results of hydrodechlorination of chlorobenzene, chloronaphthalene and chloroanthracene are given in Table 3. All the tested catalysts were found to be very effective in the removal of chlorine, with a yield of 83.0-98.5% at 260ºC. Again, differences in their porous structure do not exhibit any significant influence on the extent of dechlorination under process conditions studied in this work.

The Ni-Mo catalysts tested show a considerably higher activity compared to monometallic Ni/Al_2O_3. To achieve a comparable dechlorination degree, the latter requires a higher temperature, 350ºC [15, 29]. The susceptibility of chlorinated aromatics to dechlorination in the presence of Ni-Mo/C catalysts increases as follows: chlorobenzene< chloronaphthalene<chloroanthracene. This relation is quite surprising. Taking into account the sterical aspect only, the order is expected to be in the opposite direction. The most likely reason for this behavior is related to the degree of aromaticity of the studied compounds. The values of aromaticity indices for polyacenes decrease with increasing ring numbers [30-32]. Benzene is characterized by the strongest aromatic properties among benzenoidoic hydrocarbons.

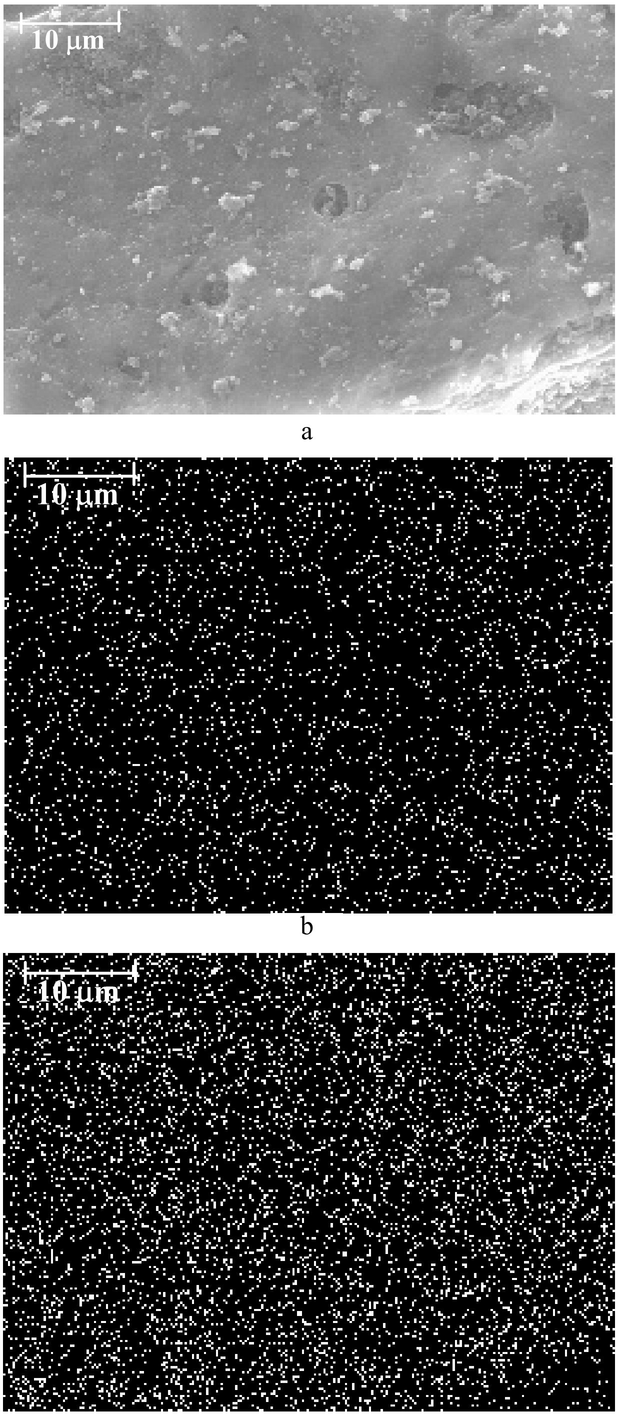

Fig. 2. SEM-EDX analysis of Ni-Mo/CN catalyst. (a) SEM image, (b) Ni distribution, (c) Mo distribution.

The same relationship can be predicted in the case of its chlorine derivatives.

Products such as cyclohexane and cyclohexane derivatives formed on hydrodechloration of chloroaromatic compounds were not observed in this work. The activation energy over catalyst is not sufficient for disruption of the resonance of aromatic ring [33, 34].

Chlorinated aromatic hydrocarbons are generally less susceptible to dechlorination compared with chloroalkanes and chloroalkenes [35]. To confirm the hypothesis that the susceptibility of monochloroaromatic hydrocarbon is related to the degree of its aromaticity, chlorocyclohexane was subjected to hydrodechlorination in the presence of tested Ni-Mo/C catalysts. The results of these experiments are included in Table 3. It can be clearly seen that chlorocyclohexane is dechlorinated with a yield over 94% at 180ºC, whereas for chlorobenzene at much higher temperatures (260ºC) the removal of chlorine is only about 83%. This observation arises from a different reaction mechanism. Dechlorination of chloroarenes is electrophilic hydrodechlorination. Dehydrochlorination of chlorocyclohexane involves intramolecular elimination E2 of HCl, where the external hydrogen source is necessary only to limit deactivation [36]. Śrębowata et al. [37] have reported that 1,2-dichloroethane can be selectively converted to ethene using activated carbon-supported Ni catalyst at 210ºC.

Conclusions

A sulphided carbon-supported Ni-Mo catalyst appears to be very effective in the hydrodechlorination of monochlorodiphenyls, chlorobenzene, chloronaphthalene and chloroanthracene. The activated carbons used as support for the Ni-Mo catalyst were characterized by a well-developed porous texture with different pore volume distribution. Pretreatment of phosphoric acid-promoted activated carbon of enhanced ash content improved the catalytic activity of resultant carbon-supported Ni-Mo catalyst due to the removal of considerable parts of inorganics left after activation. The obtained results show that 4-chlorodiphenyl is more easily dechlorinated when compared with 2-chlorodiphenyl, in which the phenyl group, in the position next to the chlorine atom, possesses a steric hindrance. Chlorobenzene homologue susceptibility to chlorine removal in the HDCl process increases as the aromatic character of the compound decreases, i.e., chlorobenzene< chloronaphthalene<chloroanthracene. A clear relationship between the porous texture of the Ni-Mo/C catalysts and chlorine removal efficiency in the HDCl reaction has been not observed in this study.

References

1. DOBSON S., Van ESCH G.J. Polichlorinated biphenyls and terphenyls. Word Health Organization, Geneva **1993**.
2. TUPPURAINEN K., HALOEN I., RUOKOJARVI P., TARHANEN J., RUUSKANEN J. Formation of PCDDs and PCDFs in municipal waste incineration and its inhibition mechanisms: a review. Chemosphere **36**, 1493, **1998**.
3. SAKAI S., HIRAOKA M., TAKEDA N., SHIOZAKI K. Behavior of coplanar PCBs and PCNs in oxidative conditions of municipal waste incineration. Chemosphere **32**, 79, **1996**.
4. VIKELSOE J., JOHANSEN E. Estimation of dioxin from fires in chemical. Chemosphere **40**, 165, **2000**.
5. PALLERLA S., CHAMBERS R.P. Reactor development for biodegradation of pentachlorophenol. Cat. Today **40**, 103, **1998**.
6. KEANE M.A., PARK C., MENINI C. Structure sensitivity in the hydrodechlorination of chlorobenzene over supported nickel. Catal. Lett. **88**, 89, **2003**.
7. KEANE M.A. Hydrodehalogenation of haloarenes over silica supported Pd and Ni. A consideration of catalytic activity/selectivity and haloarene reactivity. App. Cat. A: General **271**, 109, **2004**.
8. AMORIM C., YUAN G., PATTERSON P.M., KEANE M.A. Catalytic hydrodechlorination over Pd supported on amorphous and structured carbon. J. Cat. **234**, 268, **2005**.
9. KALNES T.N., JAMES R.B. Hydrogenation and recycle of organic waste streams. Environ. Prog. **7**, 185, **1988**.
10. BRINKMAN D.W., DICKSON J.R., WILKINSON D. Full scale hydrotreatment of polychlorinated biphenyls in the presence of used lubricating oils. Environ. Sci. Technol., **29**, 87, **1995**.
11. GIOIA F., MURENA F. Catalytic hydrodechlorination of decachlorobiphenyl. App. Cat. B: Environ. **38**, 39, **2002**.
12. GIOIA F., GALLAGHER E.J., FAMIGLIETTI V. Effect of hydrogen pressure on detoxification of 1,2,3-trichlorobenzene by catalytic hydrodechlorination with both unsulphided and sulphided Ni-Mo/γ-Al_2O_3 catalyst. J. Hazard. Mater. **38**, 277, **1994**.
13. URBANO F. J., MARINAS J. M. Hydrogenolysis of organohalogen compounds over palladium supported catalysts. Appl. Catal. A-Chemical. **173**, 329, **2001**.
14. SANTORO D., de JONG V., LOUW R. Hydrodehalogenation of chlorobenzene on activated carbon and activated carbon supported catalysts. Chemosphere **50**, 1255, **2003**.
15. MARTINO M., ROSAL R., SASTRE H., DIEZ F.V. Hydrodechlorination of dichloromethane, trichloroethylene and tetrachloroethylene over sulfided Ni/Mo-γ-alumina catalyst. App. Cat. B: Environ. **20**, 301, **1999**.
16. SANTORO D., LOUW R. Gas phase hydrogenolysis mediated by activated carbon substituted chlorobenzenes. Carbon **39**, 2091, **2001**.
17. MANION J.A., LOUW R. Relative gas-phase desubstitution rates of chlorobenzene derivates by hydrogen atoms near 1000K. J. Chem. Soc. Perkin Trans. **2**, 551, **1990**.
18. ARENDS I.W.C.E., OPHORST W.R., LOUW R., MULDER P., Gas phase hydrogenolysis mediated by activated carbon: Monosubstituted benzenes. Carbon **34**, 581, **1996**.
19. KEANE M.A., TAVOULARIS. The role of spillover hydrogen in gas phase catalytic aromatic hydrodechlorination and hydrogenation over nickel/silica. React. Kinet. Catal. Lett. **78**, 11, **2003**.
20. SUZDORF A.R., MOROZOV S.V., ANSHITS N.N., TSIGANOVA S.I., ANSHITS A.G. Gas phase hydrodechlorination of chlorinated aromatic compounds on nickel catalysts. Catal. Lett. **29**, 49, **1994**.
21. SERGUCHEV Y.A., BELOKOPYTOV Y.V. Kinetics and mechanism of the heterogeneous catalytic hydrogenolysis of chlorobenzenes and chlorocyclohexanes. Kinet. Catal. **42**, 195, **2001**.

22. KEANE M. A., PINA G., TAVOULARIS G. The catalytic hydrodechlorination of mono-, di- and trichlorobenzenes over supported nickel. Appl. Catal. B-Environ. **48**, 275, **2004**.
23. MURENA F., GIOIA F. Catalytic hydrotreating of 2,4'-DDT and 4,4'–DDT. J. Hazard. Mater. **112**, 151, **2004**.
24. SHIN E., KEANE M.A. Gas phase catalytic hydroprocessing of trichlorophenols. J. Chem. Technol. Biotechnol. **75**, 159, **2000**.
25. GRYGLEWICZ G., STOLARSKI M., GRYGLEWICZ S., KLIJANIENKO A., PIECHOCKI W., HOSTE S., Van DRIESSCHE I., CARLEER R., YPERMAN J. Hydrodechlorination of dichlorobiphenyls over Ni-Mo/Al_2O_3 catalysts prepared by spray-drying method. Chemosphere **62**, 135, **2006**.
26. GREGG, S.J., SING, K.S.W. Adsorption, Surface Area and Porosity. Academic Press, London, **1982**.
27. GaussView, Version 3.09, Semichem Inc., Shawnee Mission, KS, **2003**.
28. ZINOVYEV S.S., SHINKOVA N.A., PEROSA A., TUNDO P. Dechlorination of lindane in the multiphase catalytic reduction system with Pd/C, Pt/C and Raney-Ni. Appl. Catal. B-Environ. **47**, 27, **2004**.
29. KIM P., KIM Y., KIM H., SONG I.K., YI J. Synthesis and characterization of mesoporous alumina for use as a catalyst support in the hydrodechlorination of 1,2-dichloropropane: effect of preparation condition of mesoporous alumina. J. Mol. Catal. A: Chem. **219**, 87, **2004**.
30. Von RAGUE SCHLEYER P., MAERKER C., DRANSFELD A., Van EIKEMA HOMMES N.J.R. Nucleus-independent schifts: a simple and efficient aromaticity probe. J. Am. Chem. Soc. **118**, 6317, **1996**.
31. CYRAŃSKI M.K., KRYGOWSKI T.M. Quantitative criteria of aromaticity. Wiad. Chem. **54**, 533, **2000**.
32. MINKIN V.I., GLUKHOVTSEV M.N., SIMKIN B.Y. Aromacity and antiaromacity, electronic and structural aspect. J. Wiley and Sons, New York, **1994**.
33. CESTEROS Y., SALAGRE P.,MEDINA F., SUEIRAS J.E. Use of Ni/Al-MCM-41 catalyst for the exhaustive hydrodechlorination of 1,2,4-trichlorobenzene. Catal. Lett. **79**, 83, **2002**.
34. BALKO E.N., PRZYBYLSKI E., TRENTINI F. Exhaustive liquid-phase catalytic hydrodehalogenation of chlorobenzenes. Appl. Catal. B: Environ. **2**, 1, **1993**.
35. KIM D.I., ALLEN D.T. Catalytic hydroprocessing of chlorinated olefins. Ind. Eng. Chem. Res. **36**, 3019, **1997**.
36. TAVOULARIS G., KEANE M.A. Gas phase catalytic dehydrochlorination and hydrodechlorination of aliphatic and aromatic systems. J. Mol. Catal. A: Chemical **142**, 187, **1999**.
37. ŚRĘBOWATA A., STEFANOWICZ-PIĘTA I., JUSZCYK W., KARPIŃSKI Z. Chlorine removal from 1,2-dichloroethane over Ni/C catalysts. Polish J. Chem. **81**, 1521, **2007**.